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NIGGLI'S PRINCIPLES OF IGNEOUS PETROGENESIS

By T. N. Muthuswami, F.A.Sc.

(*Presidency College, Madras*)

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Recent advances in igneous petrogenesis are based almost entirely on the researches made at the Geophysical Laboratory, Washington. The phase relationships of various systems that are studied with improved modern technique, have given valuable insight into the possible mode of origin of rock-forming minerals from silicate melts. Valuable though such knowledge is, there remains the fact that the fundamental cause may have to be sought for in a sphere that defies experimental analysis. After all experiments are directed to determine the physical and chemical conditions that control the formation of minerals. But the genesis of minerals and their pattern are the natural outcome of a directed dynamic force.

In the organic world, a plant has its identity determined by the seed, and an animal by the egg. It would be difficult to decide how far external influences have their effects on the embryo and in what manner. Though how a seed gives rise to a particular plant and an egg to a particular animal is known, why they should do so is beyond scientific comprehension. A mineral too has its pattern determined by forces at work in the melt state.

Hence our solved problems in the laboratories are not to be considered as ends in themselves. There remain undoubtedly problems, the solutions of which are to be found only in the realm of speculation.

Niggli considers that petrogenetic causes are to be traced to reactions that take place in the melt, in other words, homogeneous equilibria conditions.

The study of petrogenetic and allied problems is usually based on the weight percentages of oxides taken as units. According to Niggli, such units cannot be anything more than the raw material which require scientific and critical treatment to discover hidden values. x grams of MgO do not correspond to x grams of Na_2O or Al_2O_3. Therefore " to combine x grams of K_2O and y grams of Na_2O to form z grams of alkali oxides, is just as meaningless as adding x grams of apples to y grams of potatoes ".

He therefore advocates that atomic and molecular values derived from the weight percentages of oxides, form the units for petrogenetic studies.

They give a correct picture of the fundamental chemical characteristic of the mineral or the rock, as a whole. They are valuable in interpreting the mode of origin of minerals, in making comparative studies of minerals and in the classification of rocks. They have the sanction of studies based on atomic chemistry.

CLASSIFICATION OF IGNEOUS ROCKS

Niggli Values.—For purposes of classification, Niggli has taken primarily into consideration:

(1) alumina,

(2) oxides of iron and magnesium,

(3) lime, and

(4) alkalies.

These four items are represented by symbols which together with the mode of calculation are given below:

(1) Determine the molecular numbers,

$$\text{Molecular numbers} = \frac{\text{weight percentage}}{\text{molecular weight}} \times 1{,}000.$$

(2) Add the molecular numbers of:

	Molecular numbers	Niggli symbols
(*a*) Al_2O_3, Cr_2O_3 and rare earths ..	m'	al
(*b*) $Fe_2O_3 \times 2$, FeO, MgO and MnO ..	n'	fm
(*c*) CaO, SrO and BaO	p'	c
(*d*) Na_2O, K_2O and Li_2O	q'	alk

The total molecular numbers of

al, fm, c and alk $= (m' + n' + p' + q') = x'$ (say)

The percentages are then determined thus:

$$\text{al} = \frac{m'}{x'} \times 100$$

$$\text{fm} = \frac{n'}{x'} \times 100$$

$$\text{c} = \frac{p'}{x'} \times 100$$

$$\text{alk} = \frac{q'}{x'} \times 100$$

In addition to these four values, other Niggli values are derived thus:

Stated on per cent. basis

$$si = \frac{\text{mol. no. of } SiO_2}{x'} \times 100$$

$$ti = \frac{\text{mol. no. of } TiO_2}{x'} \times 100$$

$$p = \frac{\text{mol. no. of } P_2O_5}{x'} \times 100$$

Stated as a ratio

$$k = \frac{\text{mol. no. of } K_2O}{alk}$$

$$mg = \frac{\text{mol. no. of MgO}}{fm}$$

Thus the molecular values—al, fm, c, alk, si, ti, and p are expressed on a percentage basis, whereas k and mg are expressed as a ratio.

qz, a derived value, known as quartz index is also used.

$$qz = si - si', \text{ where } si' = 100 + 4\,alk, \text{ when } alk < al.$$

$$qz = si - (100 + 3\,al + 1\,alk) \text{ when } alk > al.$$

qz may be positive or negative and gives valuable clue of the minerals expected to be formed.

On the basis of these values the eruptive rocks are classified into calc-alkali, soda-rich and potash-rich divisions. The divisions are subdivided into groups and magma types as mentioned below:

Calc-alkali division, into 13 groups with a total of 64 types.

Soda-rich division, into 15 groups with a total of 65 types.

Potash-rich division, into 12 groups with a total of 45 types.

One example of the calc-alkali division with the types is given below:

TABLE I

Division: Calc-alkali	Group: Hornblendite magma						
Types	si	al	fm	c	alk	k	mg
1. al-hornblendite	120	19	61	15	5	..	0·7
2. hornblendite	80	15	60	20	5	..	0·6
3. hornblende peridotite ..	80	10	74	14	2	..	0·7
4. diallagite	90	7	68	23	2	..	0·7
5. websterite	95	1	80	18	1	..	0·8

Generally alk $\leqq$ 8
al $\leqq$ 18·5
fm $>$ 50
c — 9 to 26

1.	si range ..	135—70	al about 20	c<23	
2.	si ..	135—65	al$\geqq$10	c—15 to 26	fm<70
3.	si ..	120—50	al about 12 to 7·5	c— 9 to 20	fm$\geqq$70/69
4.	si ..	120—65	al<10	c$\geqq$20	fm nearly 70, alk practically nil
5.	si	120—55	al<7·5	c— 9 to 22	fm$\geqq$70, alk practically nil

TABLE II

Molecular numbers and Atom numbers

Hornblende Norite—St. Thomas Mount, Madras

Constituents	p.c.	Mol. No.×1,000	Atom No.
SiO_2	50·04	834	834
Al_2O_3	11·65	114·5	229
Fe_2O_3	2·63	16·4	33
FeO	15·76	218·5	218·5
MnO	..	..	..
MgO	5·58	139·5	139·5
CaO	7·89	141	141
Na_2O	3·08	50	100
K_2O	0·89	10	20
TiO_2	1·93	24	24
P_2O_5	0·20	1·0	2
H_2O+	0·19	..	..
Total	99·84		Analyst—Washington

TABLE III

Calculation of Niggli Values

Niggli symbols		Molecular numbers		Niggli values
al	Al_2O_3 + Cr_2O_3 + Rare Earths 114·5 + 0 + 0 ..	115	$\frac{115}{707} \times 100$	16·27
fm	FeO + Fe_2O_3 + MgO + MnO 218·5 + 33 + 139·5 + 0	391	$\frac{391}{707} \times 100$	55·30
c	CaO + BaO + SrO 141 + 0 + 0	141	$\frac{141}{707} \times 100$	19·95
alk	K_2O + Na_2O + Li_2O 10 + 50 + 0	60	$\frac{60}{707} \times 100$	8·48
		707		100·00
si	.. ..	834	$\frac{834}{707} \times 100$	118·00
ti	.. ..	24	$\frac{24}{707} \times 100$	3·404
k	$\frac{K_2O}{K_2O+Na_2O}$		$\frac{10}{60}$	0·166
Mg	$\frac{MgO}{fm}$		$\frac{139·5}{391}$	0·357

If the rock is an eruptive one it belongs to

Group .. Hornblendite Magma } Refer values
Type .. 'Hornblendite' } already given.

If it is metamorphic it must have been derived from a calc-alumino-silicate rock with appreciable quantities of alkalies, say an alkali calc shale.

CHEMICAL EQUILIBRIUM IN MAGMATIC MELTS

Matter is said to be in equilibrium with its surroundings if it does not show any tendency to change. This condition of equilibrium is defined as a "system". A system exists as such so long as the physical and chemical conditions remain unaltered. Such equilibrium conditions may be obtained in homogeneous and heterogeneous bodies. In a homogeneous system

every part of the system has absolutely the same physical and chemical properties as every other part. An unsaturated solution of sodium chloride or a silicate melt (magma) is an example of a homogeneous system.

Heterogeneous Equilibrium.—In over-saturated conditions sodium chloride settles down from the solution. There comes a bounding surface between the solid and the solution. The physical and chemical properties of the solid are different from those of the solution. The two together constitute a heterogeneous system. This system is in equilibrium so long as the physical and chemical conditions remain the same. In the same way the moment the first mineral crystallizes from a silicate melt a new solid phase sets in, by which is meant a physically homogeneous but mechanically separable portion of a system. Thus the homogeneous system is changed to a heterogeneous system.

The mineral that crystallizes reacts with the liquid in which it is immersed, continuously or discontinuously, giving rise to additional minerals making the system more and more complex.

A systematic study of the temperatures at which synthetic minerals are in equilibrium with silicate melts of known composition is one of the set programmes of the Geophysical Laboratory, Carnegie Institute of Washington. The petrologic bearing of these studies is made out by equilibrium diagrams according to phase rule methods. The experimental facts have greatly added to the knowledge of the physico-chemical conditions relating to crystal differentiation in binary, ternary and quarternary systems. Bowen's crystallization differentiation theory has been generally accepted by distinguished petrologists all the world over. But the fact remains that the "crucible" experiments indicate only the conditions under thermodynamic equilibrium and fail to take into account "the kinetics of the processes involved in fractional crystallization".

Niggli is an advocate of Bowen's differentiation theory. But he points out "while all knowledge in this respect is unquestionably of the utmost value, the fact may not be overlooked that there must exist laws of a higher order, which govern the entire complex of phenomena".

Homogeneous Equilibrium.—Niggli searches for the cause, in the reactions that take place among the molecules while in the fluid state. An insight into the laws that govern reactions in the melt state, *i.e.*, under homogeneous equilibria conditions, would enable one to forecast what "new phase must appear during crystallization, taking place under circumstances of any kind" —(Niggli). The birth of a mineral is determined by laws that operate in the pre-birth condition,

The laboratory experiments themselves are suggestive in this regard. The metasilicate clinoenstatite ($MgSiO_3$) melts incongruently into the orthosilicate Mg_2SiO_4 at 1,557° C. There is a theoretical possibility of its further dissociation into MgO and SiO_2. Does not this suggest that the orthosilicate has very little tendency to dissociate, and lead to the hypothesis of its independent existence in the "melt"? The polysilicate orthoclase ($KAlSi_3O_8$) melts incongruently into leucite ($KAlSi_2O_6$) at 1,170° C. A still lower silicated mineral ($KAlSiO_4$) has been observed to exist in the study of the system K_2O–Al_2O_3–SiO_2. Again the dissociation of mullite ($Al_6SI_2O_{13}$) into corundum (Al_2O_3) and liquid at 1,810° C. leads to the possibility of the existence of Al_2O_3 molecule in the melt. Hence can we not postulate the potential existence of K_4SiO_4 and Na_4SiO_4 in a melt, which on combining with Al_2O_3 give rise respectively to $KAlSiO_4$ and $NaAlSiO_4$?

The emphasis is on the fact that Mg_2SiO_4, $KAlSIO_4$ and other orthosilicates such as $NaAlSiO_4$ and Ca_2SiO_4 are unstable while SiO_2 molecules are present in the melt. It is even possible that molecules such as K_4SiO_4 and Na_4SiO_4 give rise to $KAlSiO_4$ and $NaAlSiO_4$ by reacting with Al_2O_3.

Basis Molecules.—The fundamental compounds that exist in the magma are called basis molecules. There is no reason to suppose that these could be present in larger amount in a further state of dissociation. These bases on further reaction are considered to have given rise to new minerals. At this stage the following questions arise:

(i) What are the characteristics of the basis molecules?

(ii) Are the reaction equations to be balanced by weight, or by volume?

Chemical reactions are based on the principle that each element has a definite combining weight or equivalent weight, and that the combinations occur in simple multiples of these quantities. The atomic weight is either identical with the combining weight or an integral multiple of it.

Atomic weight = Equivalent weight × Valency.

Hence the atomic weight is sometimes called the combining weight.

Volume Unit.—But in petrological studies the first feature that strikes one on examining a rock megascopically or microscopically is the fabric of the rock, restricting the term "fabric" to define the sum-total of the textural and structural features of the mineral constituents. Petrogenesis seeks to explain the factors that have led to the development and proportion of minerals, as we see them in the rock. For most petrological work, the planemetric analysis is resorted to in order to give the weight percentage of

the oxides. In this analysis the volume percentage is obtained directly. Such being the case, it would be only appropriate to base reaction equations on a volume basis.

It is now an established fact that the electro-positive character of the elements is the root cause of the chemical reactions leading to mineral formation. The more electro-positive a metal is, the greater its affinity for a particular non-metal or a radical. The atomic number denotes the number of protons or of positive electricity in the nucleus of the atom. If two minerals A and B combine to form C, it may be considered as due to the atomic number of A having combined with that of B to give rise to that of C. C has an atomic number equal to the sum of the atomic numbers of A and B.

Atom Numbers as Units.—Instead of summing up the atomic numbers of the elements, there would be a justification in summing up the actual number of electro-positive atoms themselves, if the atomic numbers of the elements are the same. But they are not of course the same. However, for calculation purposes, we could consider them to be the same, and treat them all alike if the atomic numbers of the reacting elements do not vary much.

Thus the atomic number of magnesium is 12: that of silicon is 14.

$$MgO + SiO_2 \;..\;..\;.. \; MgSiO_3$$
$$12 + 14 \;..\;..\;.. \; 26$$

Or

$$1 + \frac{14}{12} \;..\;..\;.. \; \frac{26}{12}$$

If the difference $\frac{1}{6}$ is neglected, then

$$MgO + SiO_2 \;..\;..\;.. \; MgSiO_3$$
$$1 + 1 \;..\;..\;.. \; 2$$

It is interesting to note that the atomic numbers of the elements that enter into *the composition of* the rock-forming minerals show a range of 11 to 26 only as seen below:

Element	Atomic No.
Si	14
Al	13
Fe	26
Mg	12
Mn	25
Ca	20
Na	11
K	19

This range may be ignored as the actual variation in atomic numbers in all the elements taken together is 1 to 92.

Mineral Formula.—As the sum of the electro-positive elements in a molecule will give a number which denotes the maximum capacity of the molecule for reaction, it should be possible to state the formula of a mineral in a form, which besides indicating its chemical constitution would also connote its capacity for reaction.

Let us take an example. Forsterite has the composition $2\,MgOSiO_2$. Its chemical constituents are Mg, Si and O. The number of electropositive atoms are 3 (2 of Mg and 1 of Si).

(By definition, a basis molecule has only 1 electro-positive charge. Hence the basis molecule forsterite is $\frac{1}{3}\,Mg_2SiO_4$; it is given the symbol Fo.)

Thus the following table gives examples of the formulæ and symbols of a few basis molecules.

TABLE IV

Some Mineral Molecules

Mineral molecule	No. of electro-positive atoms (Cations)	Basis (Equivalent formula unit)	Symbol
Mg_2SiO_4	Mg + Si = 3 2 + 1	$\frac{1}{3}\,Mg_2SiO_4$	Fo
$KAlSiO_4$	K + Al + Si = 3 1 + 1 + 1	$\frac{1}{3}\,KAlSiO_4$	Kp
$NaAlSiO_4$	Na + Al + Si = 3 1 + 1 + 1	$\frac{1}{3}\,NaAlSiO_4$	Ne
$CaAlAlO_4$	Ca + Al + Al = 3 1 + 1 + 1	$\frac{1}{3}\,CaAlAlO_4$	Cal
SiO_2	Si = 1 1	SiO_2	Q

The formation of new minerals results thus:

(*a*) By reaction of a basis with another basis.
Example :

	Basis Kaliophyllite		Basis Quartz		Mineral Orthoclase
Symbol	Kp		Q		Or
Formula	$KAlSiO_4$	+	$2\ SiO_2$	=	$KAlSi_3O_8$
Niggli formula ..	3 Kp	+	2 Q	=	5 Or

(*b*) By reaction of a basis with a mineral.
Example :

	Basis Kaliophyllite		Mineral Orthoclase		Mineral Leucite
Symbol	Kp		Or		Lc
Formula	$KAlSiO_4$	+	$KAlSi_3O_8$	=	$K_2Al_2Si_4O_{12}$
Niggli formula ..	3 Kp	+	5 Or	=	8 Lc

(*c*) By reaction of a mineral with another mineral.
Example :

	Mineral Wollastonite		Mineral Enstatite		Mineral Diopside
Symbol	Wo		En		Di
Formula	$CaSiO_3$	+	$MgSiO_3$	=	$CaMgSi_2O_6$
Niggli formula ..	2 Wo	+	2 En	=	4 Di

The coefficients are obtained by summing up the electro-positive elements. Thus in the example (*b*):

$$3\ Kp = 1\ K + 1\ Al + 1\ Si$$
$$5\ Or = 1\ K + 1\ Al + 3\ Si$$
$$8\ Lc = 2\ K + 2\ Al + 4\ Si$$

It may also be pointed out that since

$$3\ Kp + 2\ Q = 5\ Or$$
$$30\ Kp + 20\ Q = 50\ Or$$
$$60\ Kp + 40\ Q = 100\ Or$$

and similarly in other cases. For there is a proportionate increase in the number of electro-positive atoms.

In this mode of calculation, H, C, N, O and F—elements of the first horizontal series of the periodic table—are not counted. In sulphides and halides S and Cl are not counted, as they take the place of O. But these are counted as electro-positive in sulphates and chlorates,

This principle has a great advantage in metamorphic processes. For, S, H_2O and CO_2 need not be considered, as the addition of any in a forward reaction is balanced by the escape of the same in the reverse reaction. Hence such constituents are put within brackets.

Examples.—(1) Muscovite and quartz, by metamorphism can change over to orthoclase, andalusite, and water. The reaction equations are:

Muscovite + Quartz → Orthoclase + Andalusite + Water

$KAl_3Si_3O_{10}(OH)_2 + SiO_2 \rightarrow KAlSi_3O_8 + Al_2SiO_5 + (H_2O)$

7 Ms + 1 Q → 5 Or + 3 Sil + (W)

(2) Cordierite, orthoclase and water can change over to biotite, muscovite and quartz. The reaction equations are:

Cordierite Orthoclase Water

$3\,(Mg, Fe)_2Al_4Si_5O_{18} + 8\,KAlSi_3O_8 + 8\,H_2O$

33 Cord + 40 Or + (8 W)

Biotite Muscovite Quartz

$\longrightarrow 2\,K\,(Mg, Fe)_3AlSi_3O_{10}(OH)_2 + 6\,KAl_3Si_3O_{10}(OH)_2 + 15\,SiO_2$

16 Bi + 42 Ms + 15 Q

Summary.—To summarise, chemical reactions can be conceived to take place in the melt condition. The melt is postulated to contain low silicated molecules such as Mg_2SiO_4, $KAlSiO_4$, etc. These *plus* basis molecules, by reaction, give rise to simple mineral molecules. The latter may combine among themselves, or with the basis molecules and lead to the development of other minerals. Even the growth of complex minerals can be explained by such reactions.

The reaction equations are represented in a simple manner. As the electro-positive character of the elements is directly responsible for chemical reaction, the sum of the atomic numbers of the electro-positive atoms of the reactants and that of the resulting minerals could be balanced. But as there is scarcely any difference in the atomic numbers of the elements that go to build the rock-forming minerals, no great error comes in the equation if they are balanced by taking into account the sum of the electro-positive atoms on both sides of the equation.

The basis and the mineral molecules are given symbols. Thus Q stands for quartz. Or means orthoclase. Reaction equations are made with co-efficients that denote the number of the electro-positive atoms in the consti-tuents,

Example :

$$10\,Or + 12\,En + (2\,W) \rightarrow 16\,Bi + 6\,Q.$$

According to this line of thought the oxides which are more fundamental than even the basis molecules, from the reaction point of view, should have equivalent volumes.

The following table shows that the oxides satisfy nearly this condition.

TABLE V

Rock-Forming Oxides

	Equivalent weight	Equivalent volume
SiO_2	60·1	22·7
1/2 Al_2O_3	51·0	12·9
1/2 Fe_2O_3	79·8	15·1
FeO	71·8	11·8
MnO	70·9	13·2
MgO	40·3	11·3
CaO	56·1	16·7
1/2 Na_2O	31·0	12·8
1/2 K_2O	47·1	18·2
TiO_2	79·9	18·9

The following table gives a list of 'Basis Molecules' with their respective symbols.

TABLE VI

Basis Molecule Groups

Basis (Equivalent formula unit)	Symbol	Equivalent weight	Basis (Equivalent formula unit)	Symbol	Equivalent weight
1/3 K Al Si O_4	Kp	52·7	1 Si O_2	Q	60·1
1/3 Na Al Si O_4	Ne	47·4	1 Ti O_2	Ru	79·9
1/3 Ca Al Al O_4	Cal	52·7	1 Fe S_2	Pr	120·0
1/3 Mg Al Al O_4	Sp	47·4	1 Ca F_2	Fr	78·1
1/3 Fe Al Al O_4	Hz	57·9	1/5 Ca_3 P_2O_8	Cp	62·1
1/3 K K Si O_3	Ks	51·4	1 Ca CO_3	Cc	100·0
1/3 Na Na Si O_3	Ns	40·7	1/2 CaS O_4	A	68·1
1/3 Ca Ca Si O_4	Cs	57·4	1/3 Na_2S O_4	Th	47·3
1/3 Mg Mg Si O_4	Fo	46·9	1/2 Na_2 CO_3	Nc	53·0
1/3 Fe Fe Si O_4	Fa	67·9	1/3 Fe_2Si O_5	Fs	73·2
1/3 Fe Cr Cr O_4	Cm	74·6	H_2O	W	0
1 Na Cl	Hl	116·9			
1/2 Al Al O_3	C	51·0			
1/2 Fe Fe O_3	Hm	79·8			
1/2 Zr Si O_4	Z	91·6			

It is best to remind ourselves that the aim of the study is to trace the line of development or growth of the rock as we have it for study.

This involves:

(1) The determination of the constituents either

(*a*) by the planemetric analysis and the calculation to percentage weight, knowing the specific gravity; or

(*b*) by actual chemical analysis.

(2) The compounding of the oxides to determine the basis.

(3) Compounding the basis to form the minerals *we see* which will be called katanorms.

(4) Recognising the possibility of different lines of comoination which would yield different katanorms.

(5) Finally synthesising them in such a way as to lead to the goal of modal percentage and drawing out inferences from the changes in the mineral constitution. That is, a suite of rocks may have a katanorm combination A and may also have another katanorm B or "katavariant". If two rocks in this suite have their modal percentage corresponding to A and B, a consanguinitic relationship of one to the other is established.

Or again, in a metamorphic suite, A, B and C may represent the katamezo and epizonal conditions.

Petrogenetic studies involve the searching for the cause of the katanormative variant corresponding to the modal mineral variant.

It should be obvious that Niggli's molecular norm—based on fundamental values, is adapted to bring out the relationship between chemical composition and mineral constituents of igneous and metamorphic rocks. The CIPW norm that is based on weight percentages of *hypothetical* normative minerals sometimes leads to the determination of norms not at all present in the mode. Tom F. W. Barth observes:

> "The calculation of the so-called 'norm' (CIPW norm) is a tool which, particularly for igneous rocks, has proved its great value. But in metamorphic rocks, in which the interrelation of mineralogy and chemistry is of the utmost importance, the norm classification has failed. The reason is obvious: The normalization of the different metamorphic mineral facies encounters great difficulties in a norm based on weight percentages. The chemical relations of a rock in terms of weight percentages obscure the comprehensive view; the computations, moreover, become unnecessarily cumbersome. I propose, therefore, that calculation of the classical weight norm be altogether

discontinued. I regard it as obsolete and superseded partly by the Niggli 'molecular norm', partly by the norm of the standard cell, as will be introduced in the present paper."

BASIS—RULES FOR THE CALCULATION

I. From Atom Numbers

1. Determine the molecular numbers of the constituent oxides

$$\text{Mol. No.} = \frac{\text{Weight percentage of the oxide}}{\text{Molecular weight}} \times 1{,}000.$$

2. Determine the number of atoms in each constituent from the molecular numbers as follows:

The number of atoms are obtained by multiplying the molecular numbers by 2 in the case of Al_2O_3, Fe_2O_3, Na_2O, K_2O and P_2O_5.

3. The number of atoms which may hereafter be called " atom numbers " are equal to the molecular numbers in the case of SiO_2, TiO_2, FeO, MnO, NiO, MgO, and CaO. This also holds good for H_2O.

4. The atom numbers of:

(*a*) MnO and NiO are added to FeO,
(*b*) SrO and BaO to CaO,
(*c*) Li_2O to K_2O,
(*d*) Cr_2O_3 to Al_2O_3.

5. Appreciable quantities of P_2O_5, Cl, F and S are directly converted into basis molecules.

P_2O_5 will form the basis apatite .. (Cp)
Cl will form the basis halite .. (Hl)
F will form the basis fluorite .. (Fr)
S will form the basis pyrite .. (Pr)

6. Very small quantities of the constituents can be ignored.

7. The number of atoms in each constituent is always referred to with a symbol, the first letter being in capitals thus:

(*Symbols of Atom Numbers*)

Constituents ..	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2
Symbol ..	Si	Al	Fe'''	Fe''	Mg	Ca	Na	K	Ti

Procedure

A

K

(i) Start with K and allot equivalent quantity of Al and S to make Kp which has the formula 1/3 KAl SiO_4. Thus,

$$xK + xAl + xSi = 3xKp = 3x\left[\frac{KAl\,SiO_4}{3}\right]$$

(ii) If K > Al, the balance of K after (i) is converted into the basis 1/3 K_2SiO_3 = Ks, thus,

$$yK + \frac{y}{2}\,Si = \frac{3}{2}\,yKs = \frac{3}{2}\,y\left[\frac{K_2SiO_3}{3}\right]$$

(iii) If Al remains after the saturation of K, then proceed with the calculation of basis Ne with Na.

B

Na

(i) $xNa + xAl + xSi = 3xNe = 3x\left[\frac{Na\,Al\,SiO_4}{3}\right]$.

(ii) If Na is in excess of Al, the balance of Na is converted into the basis Ns.

$$yNa + \frac{y}{2}\,Si = \frac{3}{2}\,yNs = \frac{3}{2}\,y\left[\frac{Na_2\,SiO_3}{3}\right]$$

(iii) On the other hand, if Al is in excess of Na, then turn to Ca

C

Ca

(i) $\frac{x}{2}\,Ca + xAl = \frac{3}{2}\,xCal = \frac{3}{2}\,x\left[\frac{CaAl_2O_4}{3}\right]$.

(ii) If Ca remains over after (i) above, then form Cs.

$$yCa + \frac{y}{2}\,si = \frac{3}{2}\,yCs = \frac{3}{2}\,y\left[\frac{Ca_2SiO_4}{3}\right].$$

(iii) If on the other hand, Al remains in excess, then turn to Mg

D

Mg

(i) The basis Sp is formed thus

$$\frac{y}{2}\,Mg + y\,Al = \frac{3}{2}\,ySp = \frac{3}{2}\,y\left[\frac{MgAl_2O_4}{3}\right].$$

(ii) If after Sp is formed, there is yet a balance of Al, then the saturation of Fe is taken to form the basis hercynite (Hz).

(iii) If on the other hand there is a balance of Mg proceed as directed in (G. i), after going through E and F.

E

Fe″ —

(i) $\frac{z}{2}\,Fe'' + zAl = \frac{3}{2}\,zHz = \frac{3}{2}\,z\left[\frac{Fe''\,Al_2O_4}{3}\right]$.

(ii) If still Al is in excess, corundum is formed with the balance say, *w*

$$w.\,Al = w.\,C = \frac{w.\,Al_2O_3}{2}.$$

(iii) If Fe″ is in excess, proceed as directed under (G. ii) after taking the steps F and (G. i).

F

Fe‴ —

If Fe‴ is present, then convert it to form the silicate Fs thus

$$xFe''' + \frac{x}{2}\,Si = \frac{3}{2}\,xFs = \frac{3}{2}\,x\left[\frac{Fe_2'''\,SiO_5}{3}\right].$$

G

Mg —

(i) The balance of Mg in (D.iii) is converted into the basis forsterite (Fo)

$$x.Mg + \frac{x}{2}\,Si = \frac{3}{2}\,x.\ Fo = \frac{3}{2}\,x\left[\frac{Mg_2SiO_4}{3}\right].$$

(ii) After the above step, the balance of Fe″ in E is converted into Fa as follows:

$$xFe'' + \frac{x}{2}\,Si = \frac{3}{2}\,xFa = \frac{3}{2}\,x\left[\frac{Fe_2''SiO_4}{3}\right].$$

Of the minor constituents,

(i) TiO_2 is considered as basis rutile (Ru).

(ii) ZrO_2 is combined with an equivalent amount of SiO_2 to form the basis 1/2 $ZrSiO_4$, Zircon (Z).

$$xZrO_2 + xSiO_2 = 2x\cdot Z = 2x\left[\frac{ZrSiO_4}{2}\right].$$

(iii) Lastly, the balance of SiO_2 is considered as basis Q. The other minor constituents are disposed of thus:

xP_2O_5 to form apatite (Cp) $= \frac{5}{2}\,xCp$

xCl to form halite (Hl) $= xHl$

xF to form fluorite (Fr) $= x$Fr

xS to form pyrite (Pr) $= x$Pr

xCr to form chromite (Cr) $= \frac{3}{2}x$Cr

It would therefore be possible to arrive at the following groups of combinations.

TABLE VII

Basis Groups

(*in relation to atom numbers*)

Alkali excess					
K>Al	K<Al also K+Na>Al	K+Na +2 Ca =Al	K+Na<Al also K+Na+2 Ca>Al	Al< K+Na+2 Ca +2 Fe″+2 Mg Al> K+Na+2 Ca	Al> K+Na+2 Ca +2 Fe″+2 Mg
1	2	3	4	5	6
Kp	Kp	Kp	Kp	Kp	Kp
Ks	Ne	Ne	Ne	Ne	Ne
Ns	Ns	Cal	Cal	Cal	Cal
Cs	Cs	..	Cs	Sp	Sp
Fs	Fs	Fs	Fs	Fo or Hz	Hz
Fo	Fo	Fo	Fo /	Fa	C
Fa	Fa	Fa	Fa	Fs	Fs
Ru	Ru	Ru	Ru	Ru	Ru
Q	Q	Q	Q	Q	Q

Sum up the atom numbers of all constituents.

Determine the percentage of each basis molecule as in

$$\frac{a}{s} \times 100; \quad \frac{b}{s} \times 100, \text{ etc., where}$$

$$a + b + c \ldots\ldots = s.$$

Example.—Hornblende Norite—St. Thomas Mount, Madras. (Analyst —Washington).

Calculation of the basis by distribution of atom numbers.

A glance at the atom numbers shows that

$$K + Na < Al$$

$$K + Na + 2Ca > Al$$

Hence, the basis of Group 4 will be formed.

TABLE VIII

(Hornblende Norite—St. Thomas Mount)

Basis

Constituents	Percentage wt.	Atom Nos.	Kp	Ne	Cal	Cs	Fs	Fa	Fo	Ru	Q
SiO_2	50·04	834	19·0	100		43	16·5	109·5	69·75		479·35
Al_2O_3	11·65	229	19·0	100	110						
Fe_2O_3	2·63	33·0					33·0				
FeO	15·76	219						219			
MgO	5·58	139·5							139·5		
CaO	7·89	141			55	86					
Na_2O	3·08	100		100							
K_2O	0·89	19·0	19·0								
TiO_2	1·93	24								24	
P_2O_5*	0·20	2									
H_2O	0·19	11									
Total ..	99·84	1748	57	300	165	129	49·5	328·5	209·25	24	479·35
Basis p.c. $= \times \frac{100}{1748}$			3·26	17·16	9·44	7·38	2·83	18·79	11·95	1·37	27·42
$= \times$ ·0572											99·60

* P_2O_5 —is neglected in calculation

II. From Niggli Values

The basis molecules have been derived from the atom numbers. It is possible to calculate them directly from Niggli values if they are already available.

This involves setting forth the relationship between molecular numbers used in Niggli values and the atom numbers that form the units for the calculation of the basis.

The following table gives the relationship:

TABLE IX

The Atom—The Molecule—Equations

I	II	III	IV	V
Constituents	Symbols: Atoms	Symbols: Molecules	Relationship	Reference Appendix B
SiO_2	Si	si	Si = si	
Al_2O_3	Al	al	Al = 2 al	
Fe_2O_3	Fe'''	fm	Fe = fm.(1—mg)	(1)
FeO	Fe''			
MgO	Mg	mg	Mg = fm (mg)	(2)
CaO	Ca	c	Ca = c	
Na_2O	Na	..	Na = 2 alk (1—k)	(3)
K_2O	K	k	K = 2 alk·k	(4)
TiO_2	Ti	ti	Ti = ti	

$$\Sigma = \text{si}+2\,\text{al}+\text{fm}+\text{c}+2\,\text{alk}+\text{ti}$$

$$\text{But al}+\text{fm}+\text{c}+\text{alk} = \frac{m'+n'+p'+q'}{x'} \times 100 \text{ (see p. 2)}$$

$$= 100$$

$$\therefore \quad \Sigma = \text{si}+\text{al}+\text{alk}+\text{ti}+100$$

TABLE X

Basis—Niggli Values, Equations

		Basis	Niggli values	Reference Appendix B
1/3	$KAlSiO_4$	Kp	6 alk·k	(5)
	$NaAlSiO_4$	Ne	6 alk (l−k)	(6)
	$CaAlSiO_4$	Cal	3 (al−alk)	(7)
	$CaCaSiO_3$	Cs	$\frac{3}{2}$ (c−al+alk)	(8)
	$MgMgSiO_4$	Fo	$\frac{3}{2}$ fm·mg	(9)
	$FeFeSiO_3$	Fs	$\frac{3}{2}$ fm (l−mg)	(10)
	$FeFeSiO_4$	Fa		
1	SiO_2	Q	si−(50+2 alk−al)	(11)
	TiO_2	Ru	ti	

$$\Sigma = 100+si+alk+al+ti$$

TABLE XI

Example

Calculation of the Basis from the Niggli Values

Niggli values (1)		Basis from Niggli value equations (2)		Basis percentage =(2)×100÷246 =(2)×·406 =(3)
	Kp	= 6 alk·k		
		= 6×8·48×·166	= 8·450	8·45×·406 = 3·431
si = 118·00	Ne	= 6 alk (1−k)		
al = 16·27		= 6×8·48×·834	= 42·44	42·44×·406 = 17·230
fm = 55·30	Cal	= 3×(al−alk)		
c = 19·95		= 3×(16·27−8·48)	= 23·37	23·37×·406 = 9·488
alk = 8·48				
k = 0·166	Cs	$= \frac{3}{2}$ (c−al+alk)	= 18·24	18·24×·406 = 7·404
mg = 0·360	Fo	$= \frac{3}{2}$ fm·mg		
ti = 3·40		$= \frac{3}{2} \times 55{\cdot}30 \times 0{\cdot}36$	= 29·86	29·86×·406 = 12·130
	Fs+Fa	$= \frac{3}{2}$ fm (1−mg)		
		$= \frac{3}{2} \times 55{\cdot}30 \times {\cdot}64$	= 53·09	53·09×·406 = 21·550
	Ru	= ti	= 3·40	3·40×·406 = 1·380
si	Q	= si−(50+2 alk−al)		
		= 118−(50+16·96−16·27) =	67·31	67·31×·406 = 27·330
			246·160	99·943

KATANORMATIVE MINERALS

The minerals of the basis groups are to be considered as fundamental units which have to combine with silica to form the saturated minerals. The minerals formed from the basis in the first instance, according to the prescribed rules mentioned below are called katanormative minerals or katanorms.

The katanorms thus formed may or may not be present in the rock. If they do not give us a picture of the modal percentage of the minerals, the katanorms have to be split or synthesised in such a manner that the modal percentage of minerals results out of the reaction. In this process there will be stages of growth, each stage representing a particular katanorm variant. The aim, however, is to get at the variant corresponding to the mode.

Katanorm—Rules for the Calculation

Bases	Reaction	Katanorm
3 Ns (Na, Na, SiO_3)	1. Ns is combined with an equal quantity of Fs to form: 2 Fns.	Fns (Fns) SiO_4NaFe'''
3 Ks (K, K, SiO_3)	Ks. Do. 2 Fks.	Fks (Fks) SiO_4KFe''
3 Fs (Fe_2SiO_5)	2. (*a*) 3 Fs = Fe_2SiO_5 = $Fe_2O_3+SiO_2$ = 2 Hm+1 Q	Hm—Hematite (Fe_2O_3)
	(*b*) Mt and Q will result when two units of Fs interact with one unit of Fa as follows: 6 Fs+3 Fa = $Fe_4Si_2O_{10}+Fe_2SiO_4$ = $Fe_6Si_2O_{14}$ = 2 Fe_3O_4+3 SiO_2 = 6 Mt+3 Q Therefore 2 Fs+Fa=2 Mt+1 Q	Mt—Magnetite Fe_3O_4
	(*c*) If more than two units of Fs are available for each unit of Fa, then, both magnetite (Mt) and hematite (Hm) will result as follows: Thus if x units of Fs are left over from 1, let $2y$ units of these combine with y units of Fa to form $2y$ units of Mt and y units of Q. The balance of $(x-2y)$ units of Fs will form $\frac{2}{3}(x-2y)$ of Hm and $\frac{1}{3}(x-2y)$ of Q. We therefore have	

Bases	Reaction	Katanorm
	$x \cdot Fs + y \cdot Fa$ $= (x-2y)\,Fs + y\,(2\,Fs+Fa)$ $= 2y \cdot Mt + \frac{2}{3}(x-2y)\,Hm$ $+[y+\frac{1}{3}(x-2y)]\,Q$ where $x>2y$ [*vide* (*a*) & (*b*) above]	Mt & Hm Magnetite & Hematite
	The liberated Q must be added to the originally present Q and distributed.	
3 Cal ($CaAl_2O_4$)	3. If Cal is present, anorthite is obtained. $x \cdot Cal + \frac{2}{3}xQ = \frac{5}{3}x \cdot An$	An Anorthite
3 Cs (Ca_2SiO_4)	4. If Q is present after (3), wollastonite is formed. $x \cdot Cs + \frac{1}{3}x \cdot Q = \frac{4}{3}x \cdot Wo$	Wo Wollastonite
	5. If Q is present after (4), potassic acmite (K·Ac) and Sodic acmite (Ac) are formed.	
Fks	$x \cdot Fks + \frac{x}{3}Q = \frac{4}{3}x \cdot K \cdot Ac$	Ac Acmite
Fns	$x \cdot Fns + \frac{x}{3}Q = \frac{4}{3}x \cdot Ac$	
3 Ns (Na_2SiO_3)	6. If during the formation of Fks and Fns, Ks, or Ns are left over, then, $x \cdot Ns + \frac{1}{3}xQ = \frac{4}{3}x \cdot Ns'$	Ns' Sodium-di silicate ($Na_2Si_2O_5$)
3 Ks (K_2SiO_3)	$x \cdot Ks + \frac{1}{3}xQ = \frac{4}{3}x \cdot Ks'$	Similarly Ks'
	7. If after all these operations Q still remains, then orthoclase is formed.	
3 Kp ($KAlSiO_4$)	$x \cdot Kp + \frac{2}{3}xQ = \frac{5}{3}x \cdot Or$ *or* Kp may have to be given to a balance of Q, say y, in which case $yQ + \frac{3}{2}y \cdot Kp = \frac{5}{2}y \cdot Or$	Or Orthoclase

Bases	Reaction	Katanorm
	8. For a further excess of Q albite is formed.	
3 Ne ($NaAlSiO_4$)	$yQ+\frac{3}{2}y\cdot Ne=\frac{5}{2}Ab$	Ab Albite
	9. If Sp and Hz bases are present and if there is still Q left over, cordierite (cord) is formed.	
3 Sp ($MgAl_2O_4$)	$y\cdot Q+\frac{6}{5}y\cdot Sp=\frac{11}{5}y\cdot Cord$	Cord Cordierite
3 Hz ($FeAl_2O_4$)	$y\cdot Q+\frac{6}{5}y\cdot Hz=\frac{11}{5}y\cdot Fe-Cord$	
	10. The basis molecules that are left over are Fo, Fa and C. To the extent possible,	
3 Fo (Mg_2SiO_4)	(i) Fo is converted into enstatite (En). Thus $y\cdot Q+3y\cdot Fo=4y\cdot En$	En Enstatite
3 Fa (Fe_2SiO_4)	(ii) Fa is converted into hypersthene $y\cdot Q+3y\cdot Fa=4y\cdot Hy$ and	Hy Hypersthene
2 C (Al_2O_3)	(iii) C is converted into sillimanite (Sil) $y\cdot Q+2y\cdot C=3y\cdot Sil$	Sil Sillimanite

Inasmuch as the basis is calculated to a total of 100, the new assembly of minerals will also give a total of 100.

As has been already said, the ultimate object is to get at such minerals as are actually present in the rock. In the transitional stages, the katanormative minerals may have to pass through hypothetical katavariants.

In special cases, the katamolecular norms are calculated with reference to special theoretical mineral compounds.

The mineral compounds may be made up of a basis molecule and a mineral or two minerals. The following examples are illustrative.

3 Kp + 5 Or = 8 Lc (Leucite)
3 Cal + 2 Wo = 5 Ge (Gehlenite)
3 Cal + 1 Q = 4 Ts (Tschermak's silicate)
3 Ne + 8 En $\rightleftharpoons$ 5 Ab + 6 Fo

EXAMPLE

Hornblende Norite

Calculation of the Katanorm

Basis	.. Kp	Ne	Cal	Cs	Fo	Fs	Fa	Ru	Q
Percentage	.. 3·431	17·230	9·488	7·404	12·130	2·832	18·718	1·380	27·330

Total = 99·95

Calculation		Katanorm	Used Q	Released Q
2 Fs+1 Fa	= 2 Mt+1 Q			
2·832 Fs+1·416 Fa	= 2·832 Mt+1·416 Q	Mt = 2·832	..	1·416
3 Kp+2 Q	= 5 Or			
3·431 Kp+2·287 Q	= 5·718 Or	Or = 5·718	2·287	..
3 Ne+2 Q	= 5 Ab			
17·230 Ne+11·487 Q	= 28·716 Ab	Ab = 28·716	11·487	..
3 Cal+2 Q	= 5 An			
9·488 Cal+6·325 Q	= 15·813 An	An = 15·813	6·325	..
3 Cs+1 Q	= 4 Wo			
7·40 Cs+2·46 Q	= 9·86 Wo	Wo = 9·860	2·460	..
			22·559	1·416

Total Q available $= 27\cdot330 - 22\cdot559 + 1\cdot416 = 6\cdot187.$

$$3\,Fo + 1\,Q = 4\,En$$

$$3\,Fa + 1\,Q = 4\,Hy \quad \text{for,}$$

$$1\,Q = 4\,(En + Hy)$$

$$6\cdot187\,Q = 24\cdot718\,(En + Hy)$$

$$\text{En proportional to } \frac{Fo}{Fo + Fa} \text{ (available)}$$

$$= \frac{12\cdot130}{12\cdot130 + 17\cdot302} \times 24\cdot78 = 10\cdot21$$

$$En = 10\cdot21$$

$$Hy = 14\cdot54$$

$$\text{Fo used for En} = 10\cdot21 \times \tfrac{3}{4} = 7\cdot56$$

$$\text{Fa used for Hy} = 14{\cdot}54 \times \tfrac{3}{4}$$
$$= 10{\cdot}905$$
$$\text{Fo} = 12{\cdot}130 - 7{\cdot}650$$
$$= 4{\cdot}48$$
$$\text{Fa} = 18{\cdot}718 - (10{\cdot}905 + 1{\cdot}416 \text{ for M}$$
$$= 6{\cdot}40$$
$$1\ \text{Ru} + 2\ \text{Wo} = 3\ \text{Tn}$$
$$1{\cdot}38\ \text{Ru} + 2{\cdot}76\ \text{Wo} = 4{\cdot}14\ \text{Tn}$$
$$\therefore\ \text{Tn} = 4{\cdot}14.$$
$$\text{Balance of Wo} = 9{\cdot}86 - 2{\cdot}76 = 7{\cdot}10$$
$$\text{Wo} = 7{\cdot}10.$$

Theoretical Katanorm of Hornblende Norite (1)

Katanorm	Or	Ab	An	Wo	En	Hy	Fo	Fa	Tn	Mt	Total
Percentage	5·72	28·72	15·81	7·10	10·21	14·54	4·48	6·40	4·14	2·83	99·95

The katanorm thus derived according to prescribed rules does not reflect to any great extent the mode of the rock, which is composed of andesine, diopside, ortho-pyroxenes, hornblende, and iron ores. Further, sphene, wollastonite and olivine are not present in the rock.

So an attempt must be made to evolve a katavariant which corresponds to that of the mode. In doing so, it is always desirable to take into account the actual analysis of the mineral and its volume percentage if available; a micrometric analysis indicates 20–25% hornblende.

As there is no sphene, in this case, Tn can be split back.

$$4{\cdot}14\ \text{Tn} = 1{\cdot}38\ \text{Ru} + 2{\cdot}76\ \text{Wo}$$

and the katanorm, which is really a katavariant may be rewritten as follows:—

Katavariant (2)

Katanorm	Or	Ab	An	Wo	En	Hy	Fo	Fa	Mt	Ru	Total
Percentage	5·72	28·72	15·81	9·86	10·21	14·54	4·48	6·40	2·83	1·38	99·95

Diopside can be formed thus:

$$2\,Wo + 2\,(En + Hy) = 4\,Di$$

$$9{\cdot}86\,Wo + 9{\cdot}86\,(En + Hy) = 19{\cdot}72\,Di$$

$$En \text{ in } Di = \frac{10{\cdot}21}{24{\cdot}75} \times 9{\cdot}86$$

$$= 4{\cdot}07$$

$$Hy \text{ in } Di = 5{\cdot}79$$

Deducting Wo, En and Hy used, and including Di obtained, the katanorm will be as follows:

Katavariant (3)

Katanorm	Or	Ab	An	Di	En	Hy	Fo	Fa	Mt	Ru	Total
Percentage	5·72	28·72	15·81	19·72	6·14	8·75	4·48	6·40	2·83	1·30	99·95

There is no Q to form Ho which is 20 to 25% in the mode.

Ho is obtained as follows:

$$8\,Di + 6\,(En + Hy) + 1\,Q + (1\,W) = 15\,Ho$$

Q required for about 20% Ho = 1·35.

This 1·35 Q can be liberated from Or, Ab and An, proportionately according to their availability.

TABLE XII

Ratio of Released Quartz from Feldspars

	Available from (1)	Quartz released (2)=(1)×1·35÷50·25
Or	5·72	0·154
Ab	28·72	0·771
An	15·81	0·425
Total	50·25	1·350

TABLE XIII

Ratio of Released Kp, Ne and Cal

Quartz released from	Basis	Added constituents to Ho	Constituents to be deducted from (5)	Katanorm	Katavariant =(5)−(4)
(1)	(2)	(3)	(4)	(5)	(6)
Or = 0·154	$\times \frac{3}{2}$ = 0·231 Kp	Kp = 0·231	Or = 0·385	Or = 5·72	Or = 5·33
Ab = 0·772	$\times \frac{3}{2}$ = 1·156 Ne	Ne = 1·156	Ab = 1·927	Ab = 28·72	Ab = 26·79
An = 0·425	$\times \frac{3}{2}$ = 0·638 Cal	Cal = 0·638	An = 1·063	An = 15·81	An = 14·75

Since,

$$8\ Di + 6\ (En + Hy) + 1\ Q + (1\ W) = 15\ Ho,$$

$$10{\cdot}8\ Di + 8{\cdot}1\ (En + Hy) + 1{\cdot}35\ Q + (1{\cdot}35\ W) = 20{\cdot}25\ Ho.$$

8·1 (En + Hy) is made up of 3·34 En + 4·76 Hy.

$$En = \frac{\text{available En}}{\text{available (En + Hy)}} \times 8{\cdot}1 = \frac{6{\cdot}14}{14{\cdot}89} \times 8{\cdot}1$$

$$= 3{\cdot}34$$

$$Hy = 4{\cdot}76.$$

Katavariant (4)

Katanorm	Or	Ab	An	Di	En	Hy	Ho	Fo	Fa	Mt	Ru	Total
Percentage	5·33	26·79	14·75	8·92	2·80	3·99	22·28	4·48	6·40	2·83	1·38	99·95

At this stage, it is obvious that as there is no olivine in the rock, Fo and Fa should be converted into the meta-silicates En and Hy.

The feldspars are again indented for SiO_2 required. The Kp, Ne and Cal liberated will be fixed up again in hornblende (Ho).

$$4{\cdot}48\ Fo + 1{\cdot}49\ Q = 5{\cdot}97\ En$$

$$6{\cdot}40\ Fa + 2{\cdot}13\ Q = 8{\cdot}53\ Hy$$

$$\text{Total Q} = 1{\cdot}49 + 2{\cdot}13$$

$$= 3{\cdot}62$$

3·62 Q must be taken proportionately from the available Or, Ab and An.

TABLE XIV

Ratio of further released quartz from feldspars

	Available from (1)	Quartz released (2)=(1)×3·62÷46·87
Or	5·33	0·41
Ab	26·79	2·07
An	14·75	1·14
Total	46·87	3·62

TABLE XV

Ratio of Further Released Kp, Ne and Cal

Quartz released from	Basis	Added constituents to Ho	Constituents to be deducted from (5) =(1)+(3)	Katanorm	Katavariant 6=(5)−(4)
(1)	(2)	(3)	(4)	(5)	(6)
Or = 0·41	$\times \frac{3}{2} = 0{\cdot}61$ Kp	Kp = 0·61	Or = 1·02	Or = 5·33	Or = 4·31
Ab = 2·07	$\times \frac{3}{2} = 3{\cdot}11$ Ne	Ne = 3·11	Ab = 5·18	Ab = 26·79	Ab = 21·61
An = 1·14	$\times \frac{3}{2} = 1{\cdot}71$ Cal	Cal = 1·71	An = 2·85	An = 14·75	An = 11·90

Therefore Ho (final) = 22·28 + 5·43 = 27·71.

The final katavariant values are

Katavariant (5)

Constituents	Or	Ab	An	Di	En	Hy	Ho	Mt	Ru	Total
Percentage	4·31	21·61	11·90	8·92	8·87	12·52	27·71	2·83	1·38	100·05

It may here be remarked that the necessary Q for the formation of Ho may be released by forming Bi. But in such a process, calculation shows

that there is no adequate Q for the formation of about 25 per cent. hornblende; further, it may not perhaps be quite appropriate to form Bi first and later Ho.

CALCULATION OF THE BASIS OF HORNBLENDE

The hornblende derived has a volume percentage of 27·11 and its composition is shown below:

Constituents	.. Kp	Ne	Cal	Di	En	Hy	Q	Total
As a ratio	.. 0·84	4·27	2·35	10·80	3·34	4·76	1·35	27·71

The constituents Di, En and Hy, have to be split into the bases Cs, Fo, Fa and Q as follows:

$$10{\cdot}8\ \text{Di} = 5{\cdot}40\ \text{Wo} + 2{\cdot}48\ \text{En} + 2{\cdot}92\ \text{Hy}.$$

(The ratio En : Hy is taken from the primary katanorm.)

Then, the composition will be

Constituents	.. Kp	Ne	Cal	Wo	En	Hy	Q	Total
As a ratio	.. 0·84	4·27	2·35	5·4	3·34+	4·76+	1·35	27·71
					2·48	2·92		
					5·82	7·68		

$$5{\cdot}40\ \text{Wo} = 4{\cdot}05\ \text{Cs} + 1{\cdot}35\ \text{Q}$$

$$5{\cdot}82\ \text{En} = 4{\cdot}37\ \text{Fo} + 1{\cdot}45\ \text{Q}$$

$$7{\cdot}68\ \text{Hy} = 5{\cdot}76\ \text{Fa} + 1{\cdot}92\ \text{Q}$$

Thus the bases are:

Constituents ..	.. Kp	Ne	Cal	Cs	Fo	Fa	Q	Total
As a ratio ..	.. 0·84	4·27	2·35	4·05	4·37	5·76	6·07	27·71

Inclusions of magnetite have not been taken into account in the bases.

$$\text{Mt} = 2{\cdot}83$$

Allowing approximately 1·4 Mt for the hornblende as inclusion,

$$1{\cdot}40\ \text{Fs} + 0{\cdot}70\ \text{Fa} = 1{\cdot}40\ \text{Mt} + 0{\cdot}70\ \text{Q}$$

Thus, we add in the basis of Ho 1·40 Fs and 0·70 Fa and deduct 0·70 Q.

TABLE XVI

Hornblende—Basis

Weight per cent.

Constituents	As a ratio	$\left(\frac{100}{29\cdot11} \times 3\cdot435\right)$	C.R.'s analysis
(1)	(2)	(3)	(4)
Kp ..	0·84	2·89	2·44
Ne ..	4·27	14·67	9·16
Cal ..	2·35	8·11	9·20
Cs ..	4·05	13·91	12·10
Fs ..	1·40	4·81	3·00
Fo ..	4·37	14·97	12·00
Fa ..	6·46	22·19	26·40
Q ..	5·37	18·45	23·60
Total ..	29·11	100·00	97·90, 100·00 (approx.)

It is very interesting that the calculated bases of column 3 are in close agreement with the bases given by Rajagopalan, *vide* in column 4, of hornblende from the same area.

CONCLUSION

The principles of Niggli's method outlined for the study of the origin and growth of igneous minerals and rocks is also applicable to the study of the metamorphic minerals and rocks. The genetic relationship between, say, a suite of calc gneisses with calcareous sediments or of aluminous hornfels with aluminous sediments can be cogently and intelligently established from the beginning to the end. A picture of the stages of metamorphic evolution could be drawn. The kata, meso and epizonal norms of a suite come to have great significance.

His methods are coming to be used more and more by petrologists for their interpretative studies. There is life in the variation diagrams prepared by using Niggli's fundamental units. He writes, "The resistance often met with in petrographic circles against a scientific and critical revision of analytical data probably has various causes. Beside the habit of merely taking over the analyst's figures, the fact that a choice must be made between several equally good methods of recalculating analysis-values may have produced a tendency to use none at all."

In Appendix A are given examples of reaction equations of simple and complex minerals. Some of the more important paragenetic mineral assemblages, under epi, meso and katazonal environment are also given.

To conclude, Niggli's treatment of the subject has a unique simplicity and beauty about it, as the method is directed, to understand the probable but hidden cause of the origin of minerals and rocks, before they were ushered out of the melt.

SUMMARY

Modern conceptions on the processes of crystallization of igneous rocks and the processes of recrystallization of metamorphic rocks, have resulted primarily from a knowledge of equilibrium of investigated silicate systems, which mean heterogeneous equilibria conditions. But Niggli considers that homogeneous equilibria conditions in the fluid state control mineral formation.

A critical insight into the factors that govern the formation of minerals is possible by adopting atomic and molecular units as demanded by studies in atomic chemistry. Niggli's classification of rocks is based on Molecular Values.

It has become the accepted practice to use proportions of the molecules such as SiO_2, Al_2O_3, K_2O, etc., in petrological calculations. But Niggli recommends the use of proportions of the cations (silicon and metals). The calculations are made to a total of 100.

Reaction equations are made with coefficients that denote the number of the electro-positive elements. The molecular amount of a mineral thus becomes proportional to the sum of the cations.

Niggli's view is that the modal minerals are evolved by reactions in the melt state and that therefore petrogenetic problems should be directed to get at the mode by a series of reactions. The various stages of the reaction correspond to katavariants, which finally end in a katanorm that can be equated to the mode. Igneous petrogenesis needs drastic changes. The petrographic data must be critically and scientifically studied with a view to the discovery and the expression of natural laws, reliance being placed on atomic chemistry.

ACKNOWLEDGEMENT

The writer owes deep gratitude to Professor Paul Niggli, for having gone through the manuscript and for valuable suggestions. It is a source of great encouragement to hear from the distinguished petrologist that the contribution is "an interesting and useful introduction to this

important aspect of petrographic technique, and will be of help to petrographers both in India and elsewhere".

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APPENDIX A

IMPORTANT ROCK-FORMING MINERALS

Polysilicates

Orthoclase ..	Or	3 Kp + 2 Q = 5 Or	(1)
Albite ..	Ab	3 Ne + 2 Q = 5 Ab	(2)
Anorthite ..	An	3 Cal + 2 Q = 5 An	(3)

Metasilicates

Leucite ..	Lc	3 Kp + 1 Q = 4 Lc	(4)
Wollastonite ..	Wo	3 Cs + 1 Q = 4 Wo	(5)
Hypersthene ..	Hy	3 Fa + 1 Q = 4 Hy	(6)
Enstatite ..	En	3 Fo + 1 Q = 4 En	(7)
Diopside ..	Di	2 Wo + 2 En = 4 Di	(8)
Hedenbergite ..	Hed	2 Wo + 2 Hy = 4 Hed	(9)
Acmite } Aegerine } ..	Ac	3 Ns + 2 Hm + 3 Q = 8 Ac	(10)
Jadeite ..	Jd	3 Ne + 1 Q = 4 Jd	(11)
Augite .. (special composition)	Aug	4 Di + 3 Sp + 1 Q = 8 Aug	(12)
Hornblende ..	Ho	8 Di + 6 En + 1 Q + (1 W) = 15 Ho	(13)
Cordierite ..	Cord	6 Sp + 5 Q = 11 Cord	(14)
	Fe-Cord	6 Hz + 5 Q = 11 Fe-Cord	(15)

Orthosilicates

Cancrinite ..	Canc	18 Ne + 2 Cc = 20 Canc	(16)
Sodalite ..	Sod	18 Ne + 2 Hl = 20 Sod	(17)
Hauynite ..	Hau	18 Ne + 4 A = 22 Hau	(18)
$CaSO_4$ anhydrite ..	A		
Nosean ..	Nos	18 Ne + 3 Th = 21 Nos	(19)
Na_2SO_4 thenardite	Th		
Grossularite ..	Gro	5 An + 3 Cs = 8 Gro	(20)
Pyrope ..	Pyp	11 Cord + 8 En = 16 Pyp + 3 Q	(21)
Almandite ..	Alm	11 Fe-Cord + 8 Hy = 16 Alm + 3 Q	(22)
Andradite ..	Andr	6 Wo + 2 Hm = 8 Andr	(23)
Forsterite ..	Fo	Basis	(24)

Fayalite	Fa	Basis	(25)
Larnite	Cs	Basis	(26)
Monticellite	Mont	3 Cs + 3 Fo = 6 Mont	(27)
Meionite	Me	15 An + 1 Cc = 16 Me	(28)
Marialite	Ma	15 Ab + 1 Hl = 16 Ma	(29)
$3NaAlSi_3O_8$—NaCl			
$3NaAlSi_3O_8$ $\frac{1}{2}Na_2SO_4$		30 Ab + 3 Th = 33 Ma	(30)
$3NaAlSi_3O_8$ $\frac{1}{2}Na_2CO_3$		30 Ab + 2 Nc = 32 Ma	(31)
Gehlinite	Ge	3 Cal + 2 Wo = 5 Ge	(32)
Akermanite	Ak	3 Cs + 2 En = 5 Ak	(33)
Vesuvianite $Ca_{10}Al_4(Mg, Fe)_2Si_9O_{34}(OH, F)_4$	Ves	18 (Cs, Fo) + 6 Sil + 1 Q + (2 W) = 25 Ves	(34)
Sillimanite / Andalusite / Kyanite	Sil	2 C + 1 Q = 3 Sil	(35)
Zoisite	Zo	9 Cal + 2 Wo + 5 Q + (1 W) = 16 Zo	(36)
Epidote	Ep (*l*) = Fe-Ep	6 Cal + 4 Wo + 2 Hm + 4 Q + (1W) = 16 Ep (*l*)	(37)
Analcite	Anc	4 Jd + (1 W) = 4 Anc	(38)
Staurolite	Staur	3 Hz + 3 Sil + 1 Q + (1 W) = 7 Staur	(39)
Muscovite	Ms	10 Or + 4 C + (2 W) = 14 Ms	(40)
Biotite	Fe-Bi	6 Kp + 9 Fa + 1 Q + (2 W) = 16 Bi	(41)
Phlogopite	Mg-Bi= Pgp	6 Kp + 9 Fo + 1 Q + (2 W) = 16 Pgp	(42)
Siderophyllite $(H_4K_2Fe_5Al_4Si_5O_{24})$	Sdro	6 Kp + 10 Hy + 3 Sil + (2 W) = 16 Sdro + 3 Q	(43)
Chloritoid / Ottrelite	Ottr	3 Hz + 1 Q + (2 W) = 4 Ottr	(44)
Serpentine	Serp	3 Fo + 2 En + (2 W) = 5 Serp	(45)
Talc	Tc	6 En + 1 Q + (1 W) = 7 Tc	(46)
Kaolin	Ka	3 Sil + 1 Q + (2 W) = 4 Ka	(47)
Titanite	Tit	1 Ru + 2 Wo = 3 Tit	(48)

Tschermak Silicates

$CaAl_2SiO_6$ ..	Ts	3 Cal + 1 Q = 4 Ts	(49)
$MgAl_2SiO_6$ ..	Mg-Ts	3 Sp + 1 Q = 4 Mg-Ts	(50)

EXAMPLES OF COMPLEX REACTIONS

Paragenetic Associations

A. Epizonal Minerals

1. *Serpentinization* — 6 Fo + (2 W) + (CO_2) = 5 Serp + 1 Mgs (51)

   Magnesite .. Mgs — 9 Fo + 1 Q + (4 W) = 10 Serp (52)

   Periclase .. Ps — 15 Fo + (4 W) = 10 Serp + 4 Ps + 1 Q removed in solution (53)

2. *Steatization* .. — 10 Serp + (3 CO_2) = 7 Tc + 3 Mgs + (2 W) (54)

   (Grammatite) Gram
   Tremolite — 15 Gram + (4 CO_2) = 4 Dol + 7 Tc + 4 Q (55)
   Dolomite .. Dol

3. *Steatization—Carbonatization* — 10 Serp + (6 CO_2) = 3 Mgs + 7 Tc + (3 CO_2) + (2 W)
   or 6 Mgs + 4 Q + (4 W) (56)

4. *Kaolinization*

   Kaolin .. Kaol
   Potas. Carbonate Kc — 30 Or + (6 W) + (3 CO_2) = 12 Kaol + 6 Kc + 12 Q (57)

5. *Albitization* .. — 5 An + 2 Nc + 4 Q = 10 Ab + 1 Cc (58)

   Sodium Carbonate Nc

Epi-Mesozonal Minerals

6. *Decarbonization* (Progressive) — 6 Dol + 4 Q + (W) = 7 Tc + 3 Cc + (3 CO_2) (59)

   14 Tc + 3 Cc = 15 Ho + 2 Dol + (CO_2) + (H_2O) (60)

Carbonization .. $3\,Cc + 8\,Bi + 6\,Q = 12\,Di + 5\,Or + (1\,W) + 3\,CO_2$ (61)

Mesozonal Minerals

Anthophyllite .. Anth $45\,Anth + 56\,Di + 4\,Q + (4\,W) = 105\,Ho$ (62)

Tremolite .. Ho

Almandite .. Alm $8\,Hy + 11\,Fe\text{-}Cord = 16\,Alm + 3\,Q$ (63)

$8\,Fe\text{-}Bi + 6\,Sil + 1\,Q = 7\,Ms + 8\,Alm$ (64)

Staurolite .. Staur $8\,Alm + 15\,Sil + (1\,W) = 21\,Staur + 2\,Q$ (65)

Muscovite .. Ms. $8\,Fe\text{-}Bi + 21\,Sil + (W) = 7\,Ms + 21\,Staur + 1\,Q$ (66)

$11\,Fe\text{-}Cord + 2\,Hm + (W) = 7\,Staur + 3\,Mt + 3\,Q$ (67)

Katazonal Minerals

Forsterite .. Fo $4\,Dol + 1\,Q = 2\,Cc + 3\,Fo + (2\,CO_2)$ (68)

Cordierite .. Cord $42\,Ms + 16\,Bi + 15\,Q = 40\,Or + 33\,Cord + (8\,W)$ (69)

Sapphirinization

Sapphirine .. Sphr $3\,Fo + 12\,En + 16\,C + 1\,Q = 11\,cord + 21\,Sphr$ (70)

Sillimanite .. Sil $10\,An + 12\,Fo + 4\,Di + 3\,Q = 8\,Gro + 18\,(En + Hy) + 3\,Sil$ (71)

Enstatite .. En $10\,An + 18\,Fo + 4\,Di + 3\,Q = 8\,Gro + 3\,Sp + 24\,En$ (72)

Pyrope .. Pyr $10\,An + 16\,En = 16\,Pyp + 8\,Di + 2\,Q$ (73)

Spinel .. Sp $5\,An + 4\,Di = 3\,Sp + 4\,Wo + 2\,Q$ (74)

Sapphirinization .. $15\,An + 28\,En + 12\,Wo + 36\,Sp + 5\,Q + (2\,W) = 30\,Anth + 42\,Sphr + 24\,Gro$ (75)

Phlogopitization

Phlogopite .. (Mg-Bi) Pyp $18\,Sp + 20\,En + 4\,Q + 4\,KO_{\frac{1}{2}} + (4\,W) = 14\,Sphr + 32\,Mg\text{-}Bi$ (76)

APPENDIX B

$fm = FeO + 2\,Fe_2O_3 + MgO$

$Fe = FeO + 2\,Fe_2O_3$

$Fe = fm - MgO$

$mg = \frac{MgO}{fm}$

$Fe = fm - fm \cdot mg$

$Fe = fm\,(1 - mg)$ (1)

$mg = \frac{MgO}{fm}$ or $\frac{Mg}{fm}$

$Mg = fm \cdot mg$ (2)

$alk = Na_2O + K_2O$

$k = \frac{K_2O}{Na_2O + K_2O}$

$Na_2O = alk - K_2O$

$K_2O = k\,(K_2O + Na_2O)$

$= k \cdot alk$

$Na_2O = alk - k \cdot alk$

$= alk\,(1 - k)$

$Na = 2\,alk\,(1 - k)$

[Na_2O — molecular number to be multiplied by 2 to get atom numbers. alk $(1 - k)$ is molecular number.] (3)

$K_2O = k \cdot alk$

$K = 2\,alk \cdot k$

(K_2O — molecular numbers to be multiplied by 2 to get atom numbers. $k \cdot alk$ value is in molecular numbers.) (4)

$K = 2\,alk \cdot k$

$Kp = 3\,K = 6\,alk \cdot k$ (5)

$$\text{Na} = 2\,\text{alk}\,(1-\text{k})\ \text{(see 3)}$$

$$\text{Ne} = 3\,\text{Na}$$

$$\text{Ne} = 6\,\text{alk}\,(1-\text{k}) \qquad (6)$$

Atom numbers of Al_2O_3 are distributed to CaO, only after satisfying K_2O and Na_2O.

$$\text{Available Al} = 2\,(\text{al}-\text{alk})$$

(1)

$$\text{Cal} = \frac{3}{2}\,\text{Al}$$

$$= 3\,(\text{al}-\text{alk}) \qquad (7)$$

(2)

Cs is formed from CaO, left over after CaO allotment to Cal

Ca allotted to Cal = al − alk

Ca balance for Cs = (c − al + alk)

$$\text{Cs} = \frac{3}{2}\,(\text{c}-\text{al}+\text{alk}) \qquad (8)$$

$$\text{Fo} = \frac{3}{2}\,\text{Mg atoms}$$

$$= \frac{3}{2}\,\text{fm}\cdot\text{mg}\ \text{(see 2)} \qquad (9)$$

$$\text{Fe} = \text{fm}\,(1-\text{mg}) \qquad (\textit{see}\ 1)$$

(3)

$$\text{Fs} + \text{Fa} = \frac{3}{2}\,\text{fm}\,(1-\text{mg})$$

Fs + Fa contain each

$\frac{3}{2}$ Fs and Fa atoms respectively. (10)

$$\text{Q} = \text{si} - (50 + 2\,\text{alk} - \text{al})$$

(4)

This value of Q is obtained as follows:

Q is the balance of atoms left over after forming the other bases.

(5)

Total available atoms

= si + 100 + al + alk + ti (*see* Table IX) (*a*)

Total atoms distributed to basis molecules

$$= 3\,\text{alk} + \frac{3}{2}\,\text{al} + \frac{3}{2}\,\text{c} + \frac{3}{2}\,\text{alk} + \frac{3}{2}\,\text{fm} + \text{ti}$$

$$= 3\,\text{alk} + \text{ti} + \frac{3}{2}\,(\text{al} + \text{c} + \text{alk} + \text{fm})$$

Since $\text{al} + \text{c} + \text{alk} + \text{fm} = 100$

$$= 3\,\text{alk} + \text{ti} + \frac{3}{2} \times 100$$

$$= 3\,\text{alk} + \text{ti} + 150 \qquad (b)$$

Deducting (*b*) from (*a*)

$$\text{si} - 50 - 2\,\text{alk} + \text{al}$$

$$\therefore\ \text{Q} = \text{si} - (50 + 2\,\text{alk} - \text{al}) \qquad (11)$$

HIGH ALTITUDE BALLOON EXPERIMENTS AND MEASUREMENT OF THE HEAVY PRIMARY RADIATION FLUX AT THE GEOMAGNETIC EQUATOR

By H. J. Taylor, F.A.Sc., M. Sitaramaswami
and
P. N. Krishnamoorthy
(Tata Institute of Fundamental Research, Bombay)

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1. Introduction

The flux and charge spectrum of heavy primary cosmic radiation has been studied by several workers by exposing nuclear emulsions at high altitudes, and geomagnetic latitudes from 30° N. to 55° N. (Bradt, *et al.*, 1950 *a*; Dainton, *et al.*, 1950; Freier, *et al.*, 1951). To obtain the integral energy spectrum of the primaries, it is necessary to extend these observations to other latitudes. The present paper reports experiments made for this purpose near the geomagnetic equator. Flights were made from Tambaram, near Madras, and from Bangalore, during October and November, 1950. Both places have geomagnetic latitude 3° N. A summary of the flight data is given in Table I.

Table I

Summary of Flight Data

Flight number	Launched from	Date of launching	Maximum height reached in ft.	Plates flown	Remarks
1	Tambaram	15–10–1950	40,000	NT4–250μ	Main line gave way about 50 min. after launching
2	,,	20–10–1950	76,600	G5–500 μ	Plates developed at Bristol
3	,,	22–10–1950	79,400	NT4–250 μ	Plates developed at Bombay
4	,,	29–10–1950	81,300	NT4–250 μ	,, ,,
5	,,	31–10–1950	50,000	G5–500 μ	Plates flown again in flight 9
6	,,	5–11–1950	52,700	NT4–250 μ	Plates flown again in flight 7
7	,,	8–11–1950	79,600	NT4–250 μ	Plates developed at Rochester
8	,,	18–11–1950	81,100	G5–500 μ	Plates lost at sea
9	,,	23–11–1950	..	G5–500 μ	,, ,,
10	,,	26–11–1950	94,500	G5–500 μ	Highest flight in series. Plates lost at sea
11	Bangalore	7–12–1950	84,700	Brass Stack	Plates developed at Rochester
12	,,	8–12–1950	91,800	Brass Stack	Balloon break-up. Plates used again in flight 13
13	,,	9–12–1950	62,700	Brass Stack	Plates not recovered

One object of these experiments was to study the E.-W. asymmetry of the heavy primary radiation, which has not yet been measured. For this purpose a servomechanism was designed to maintain the plates during flight in a fixed orientation. Kodak NT4–250 μ and Ilford G5–500 μ were the types used. In a typical flight a stack of 80 plates was used, each 3″ by 8″, placed vertically with the plane of the plates perpendicular to the magnetic meridian. To study the spectrum of the high-energy primaries the "brass stack" was employed. This consists of 20 horizontally stacked plates, individually sandwiched between brass plates of 3 mm. thickness. The plates are positioned with great accuracy. The heavy primaries interact principally with the brass, forming narrow showers of break-up products which can be followed through successive plates. Either the opening angle of such showers or the relative scattering of evaporation alpha particles and heavier fragments can be used to determine the energy of the primary (Kaplon, *et al.*, 1952).

Plates exposed at high altitudes record large π-meson showers of high energy similar to the "R" shower (Bradt, *et al.*, 1950 *b*). The study of the development of soft cores in such showers enables one to place an upper limit on the lifetime of the neutral π-meson (Kaplon, *et al.*, 1952).

The objects of these experiments have not been fully realised, but values of the flux have been obtained for the C-N-O group of primaries and for the group with $Z > 10$. The detailed altitude curves have also yielded new information on the behaviour of high-altitude balloons.

2. The Orientation Unit

Fig. 1 shows the orientation unit with the plate box in position. The dome on the right goes over the unit, and is bolted to the circular base. A rubber gasket makes the assembly airtight, so that normal pressure is maintained inside during the flight. The dome is of aluminium and is painted black.

The photograph shows the batteries (A), the electronic circuit (B), the plate box (C), the compass box (D), and the monitor (E). Fig. 2 shows the circuit diagram. The ends of a compass needle are provided with wires dipping into semicircular troughs of water which form part of an impedance bridge, to which the output of a 1,000-cycle oscillator is applied. A deviation of the needle results in a signal whose phase depends on the direction of the deviation. The signal actuates a servomotor which rotates the plate assembly in such a direction as to annul the deviation. The initial balance is brought about by adjusting the two potentiometers. Thereafter the

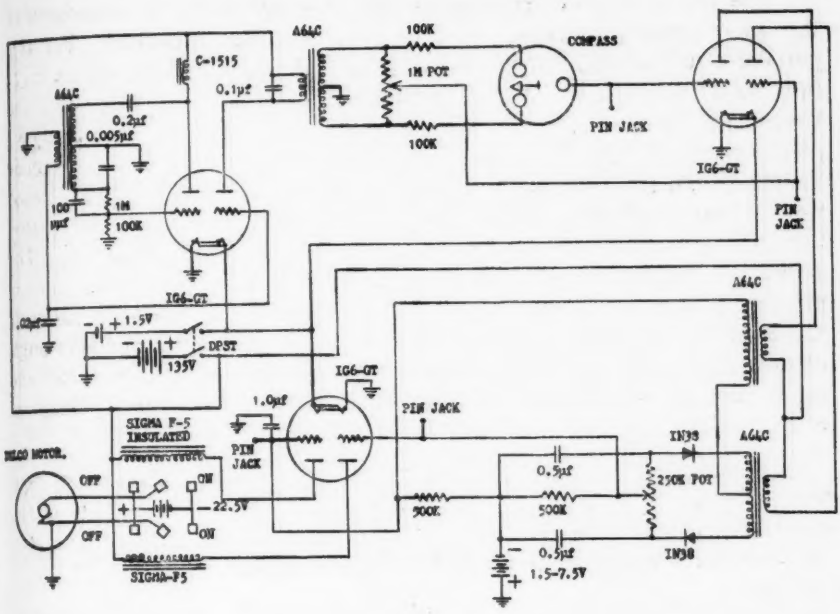

FIG. 2

orientation of the plate assembly is maintained, provided the rate of rotation of the gondola is not more than about three revolutions per minute. The apparatus showed no tendency to 'hunt' or to maintain the gondola in oscillation, and with careful preliminary adjustment it behaved well in practice.

The monitor consists of a magnetic needle horizontally pivoted and centrally mounted in a flat circular box. The needle carries a polonium source at one end, and a circular piece of Kadak NTB 3-35μ film is mounted inside the lid of the box to record alpha particles from the source. On descent the rapid downward acceleration causes the lid to fly open. It is then held by a catch, so that no further irradiation of the film occurs to confuse the record. The distribution of alpha particle tracks on the film indicates the degree to which orientation has been maintained during the flight. In flights where the apparatus was recovered intact the monitor record showed that orientation had been maintained within about $\pm$ 15°. A magnetic orientation unit of similar design has recently been described in detail (Golian and Reilly, 1951).

3. BALLOON TECHNIQUE

Dewey and Almy balloons were used for these flights, the types being K 2,000, J 2,000, J 800 and J 1,400. K balloons are of latex (natural rubber), and J balloons of neoprene (plastic). The number indicates the nominal weight of the balloon, but there are large individual variations. K balloons require no pretreatment, but J balloons, in accordance with manufacturer's instructions, are heated for a few minutes in nearly boiling water shortly before filling. Many balloons are uneven, and develop bulges or blisters on filling, but there is no evidence that these defects appreciably weaken the balloons.

Balloons are filled from hydrogen cylinders through a flexible hose, until they just pick up a pre-determined load. Considerable errors are possible in judging the precise moment when the load is balanced, particularly when there is any wind. Cooling takes place as the hydrogen expands through the nozzle, and as the balloon warms up there is a noticeable increase of lift. It is therefore difficult to achieve accurately the desired lift, the uncertainty being of the order of 10% either way.

Each flight is planned for a definite rate of rise, given by the empirical formula

$$R = 1{\cdot}34\,\frac{\sqrt{F} - g}{\sqrt[3]{F} + B},$$

where R is the rate in 1,000 ft./min., F is the weight the balloon will just pick up at the ground, g the external load per balloon during flight, and B the balloon weight, all in kg. The formula holds reasonably well for balloons attached separately to a long line; but it is not applicable to balloons in large clusters, where the rate of rise is noticeably less than given by the formula. High rates of rise (800 to 1,200 ft. per min.) appear to be associated with a high probability of balloon failure, especially between 35,000 and 50,000 ft., where turbulent motion is often very evident.

The necessary hydrogen was produced as required in standard generators by means of ferrosilicon and caustic soda. By connecting cylinders to the generators it was possible to use double the normal charge. The first generator was used to fill one empty cylinder to a pressure of 900 lb./sq.in., and another to 300 lb./sq.in. The next charging filled the first cylinder to the full pressure of 1,400 lb., and the second to 800 lb. The third charge filled the second cylinder to the full pressure and an empty cylinder to 300 lb. By repeating this process, five workers could fill 20 cylinders in about 16 hours, using 15 generators. Previously the generators have been used to fill balloons directly, but the present method is more

advantageous and involves fewer generators. It does not appear to have been used before in India.

Balloons on 35-foot strings were attached individually or in small clusters to a long nylon line at 35-foot intervals. Clusters of 3 to 7 balloons were used in different flights. In flight 12, 12 balloons on 80-foot strings and 11 on 60-foot strings were flown as a single two-layer cluster. Most of these survived to a height of 92,000 ft., when atleast a dozen burst simultaneously. In this case the central balloons would, when fully expanded, be pressed tightly together, and the failure of a single balloon would endanger all the others.

The equipment was attached to the lower end of the line in the order (1) clock release, set to detach the load at a predetermined time, (2) parachute, (3) the gondola carrying the orientation unit, (4) barograph, (5) ballast. The clock release was used only in the earlier flights. The purpose of the ballast is to reduce the initial rate of rise, and to compensate for loss of lift as balloons burst. In the earlier flights 8 kg. of sand, running at the rate of 1·2 kg. per hour, was used as ballast. In later flights hot water was used successfully.

The launching of a 400-foot line, carrying upto 32 balloons, and with equipment weighing upto 40 kg., presented some problems. The method adopted was to hold both ends of the line, with the top end to windward of the load, and allow the central balloons to lift the line into a vertical arc. The top end was then released. When the line was approximately vertical the load was released. In this way it was possible to avoid the danger of the load being dragged along the ground by an inclined balloon line.

4. Altitude Measurements

In flight 11 a recording aneroid barometer was used. This gave an excellent record, reproducing the details of the trigonometrically determined path with great fidelity, but the absolute calibration was uncertain. On other flights a specially designed mercury barograph was used, in which the movement of the mercury meniscus is photographed on a revolving drum. Illumination was provided either by a 2-volt lamp working on batteries, or by daylight. Unfortunately the barograph was tampered with by the finders on several occasions, and developed defects on others, with the result that only one satisfactory record was obtained, for flight 4, which again agrees very well with the trigonometrical trajectory.

The altitude curves for these flights are therefore based entirely on the trigonometrical data obtained from theodolite stations. For the Tambaram

flights five permanent stations were used: Tambaram, Meenambakkam (6 miles N.E.), Vellore (67 miles W.), Kolar (125 miles W.), and Bangalore (177 miles W.). The locations were known with precision, and the three distant stations were in continuous touch with Tambaram by two-way short-wave radio. Synchronised measurements of altitude and azimuth were made at five-minute intervals during the flights. For the Bangalore flights, the theodolites at Bangalore and Kolar were used. On the last flight the balloons were followed across country by a mobile party taking theodolite readings from various locations, making azimuth corrections by reference to map positions and sun observations. The resultant altitude curves have been computed by an analysis of all the observations available. These curves are shown in Fig. 3.

5. Floating Levels of Balloon Systems

The detailed altitude-time curves obtained for these flights have revealed an important feature of balloon behaviour which has not been previously reported. As the flight rises balloons progressively burst until approximate equilibrium is reached. The system then shows a series of stable floating levels, which may be maintained for considerable periods. In Fig. 3, flight 13 shows a single level maintained with very small variations for 9 hours. Flights 3 and 4 show cases where the system of balloons falls suddenly from one level to another, three such levels being clearly shown in flight 4. When ballast is steadily running a 'level' becomes a steady increase of height with time, but the discrete set of 'levels' is still apparent, as in flights 8 and 10. The sudden fall from one level to another is almost certainly caused by the bursting of a balloon, but owing to the great distances at which the balloons were observed this could not always be checked observationally.

In previous studies it has always been assumed that the pressures inside and outside a balloon are equal, and that "the effects of pressure created by the elastic contraction of the rubber balloon fabric.... may be neglected" (Clarke and Korff, 1941). On this assumption the lift due to the hydrogen is independent of the pressure. If the total lift is greater than the load the balloon rises indefinitely, otherwise it descends to the ground. A group would behave in the same way as a single balloon, and could only float if the lift happened exactly to equal the load. Even so there could be no floating level, for there would be equilibrium at all heights.

The existence of stable floating levels contradicts the above assumption. We have to take into account a contribution p_1 to the internal pressure given by

$$p_1 = 2T/r, \qquad (1)$$

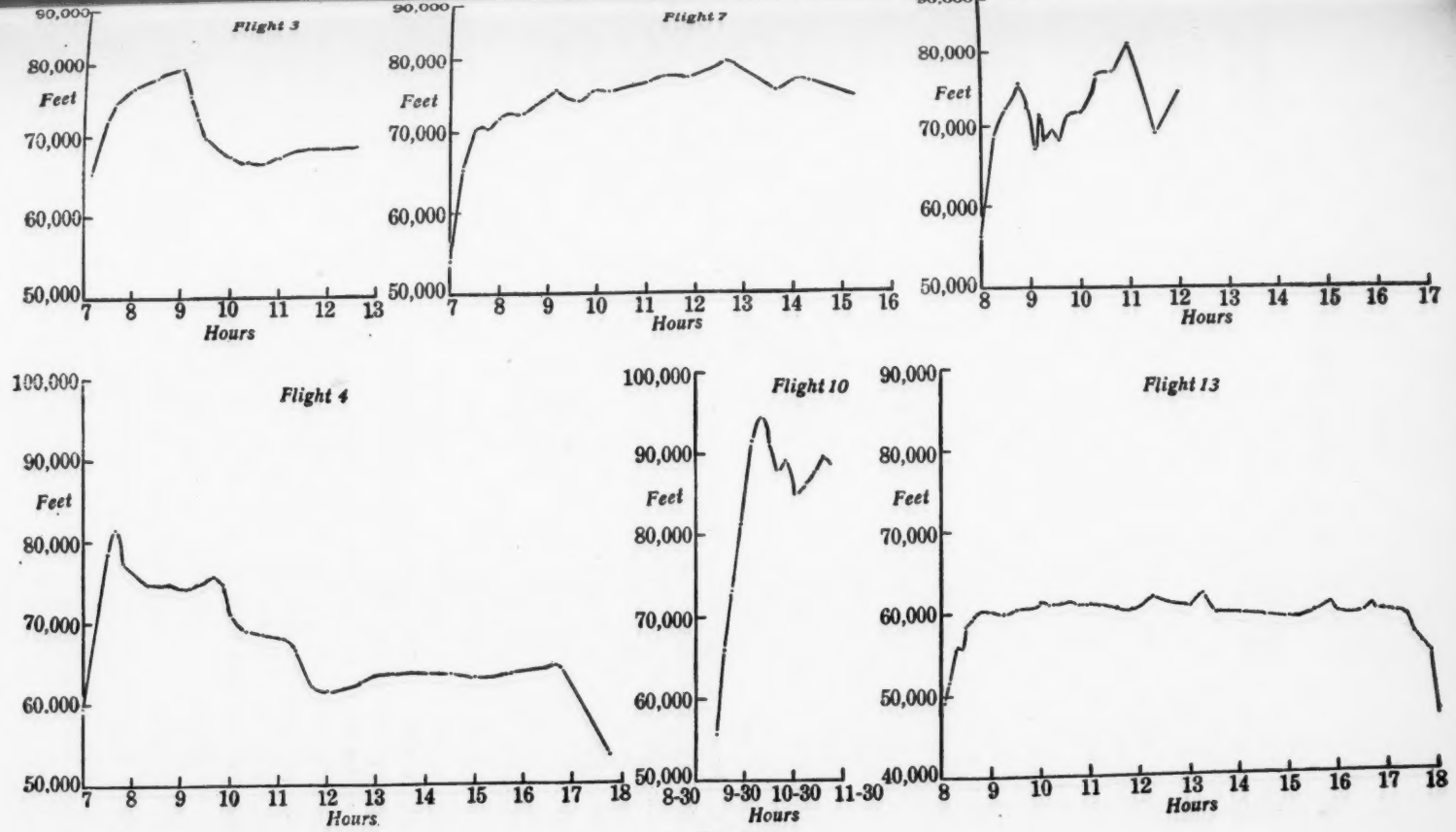
Flight 3
Flight 7
Flight 4
Flight 10
Flight 13
Feet
Hours
90,000
80,000
70,000
60,000
50,000
100,000
40,000
7 8 9 10 11 12 13
7 8 9 10 11 12 13 14 15 16
8 9 10 11 12 13 14 15 16 17
7 8 9 10 11 12 13 14 15 16 17 18
8-30 9-30 10-30 11-30
8 9 10 11 12 13 14 15 16 17 18

FIG. 3

where T is the tension in the rubber and r the radius of the balloon. At the ground p_1 is of the order of a millibar and is negligible, but it becomes increasingly important, both absolutely and relatively, as the balloon expands. Rubber balloons blown up on the ground show a minimum value of p_1 at moderate inflation, followed by an increase which is roughly proportional to the volume. This suggests that at high altitudes the elastic contribution to the internal pressure might reasonably be represented by the equation

$$p_1 = p_0 + k/p, \tag{2}$$

where p is the external pressure and p_0, k are constants for a given type of balloon.

We adopt the following notation:

m = mass of hydrogen in a balloon,

V = volume of balloon,

T = the absolute temperature of the surrounding air,

t = excess internal temperature of the balloon,

M_H, M_A = molecular weights of hydrogen and air,

W = total load (= hydrogen + rubber + payload),

$L = W/m$ = load per gram of hydrogen,

R = gas constant per mole.

The volume is given by $V = (m/M_H)\,R\,(T + t)/(p + p_1)$

The density of the air is $M_A p/RT$

The upthrust is thus $m\,(M_A/M_H)\,(1 + t/T)/(1 + p_1/p)$

At a floating level this must be equated to W. Hence

$$(M_A/M_H)\,(1 + t/T)/L = 1 + p_1/p$$

The value of t is unknown but must be appreciable, since the balloon is exposed to the sun's radiation, and a system of balloons always loses lift very quickly at sunset. A fair estimate appears to be $t/T = 0{\cdot}11$. With $M_A/M_H = 14{\cdot}4$ the equation becomes

$$16/L = 1 + p_1/p. \tag{3}$$

If we assume the validity of equation (2) the equilibrium equation becomes

$$16/L = 1 + p_0/p + k/p^2 \tag{4}$$

This equation is plotted in Fig. 4 for the values p_0=2 mb. and $k = 100$. These values have been chosen to give a reasonable fit with the observations.

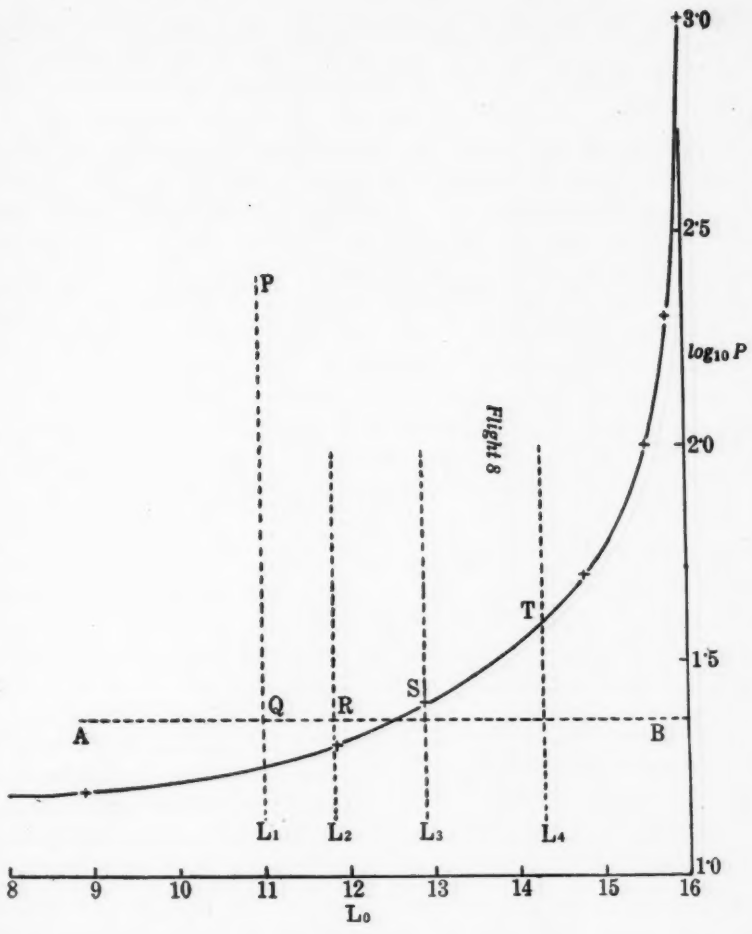

FIG. 4

Initially a system of balloons has a definite load per gram of hydrogen, say L_1, which remains constant as long as the balloons remain intact. The rise of the balloons is therefore represented in Fig. 4 by the line PQ. AB represents the bursting level, at which a balloon reaches its maximum distension. At Q one balloon bursts. *m* grams of hydrogen are lost, and W decreases by the weight of the hydrogen and the rubber which falls off. L changes discontinuously to L_2, and the representative point on the diagram is now R. As R is still below the equilibrium level another balloon will

burst. The new value of L is L_3, for which the system is above the equilibrium level. It therefore falls to S, and if another balloon bursts, to T. As S and T are below the bursting level the system may persist for long periods at these levels.

The points Q, R, S, T in Fig. 4 have been computed for a flight of 10 balloons weighing 1·4 kg. each, inflated to a diameter of 1·9 m. or to a lift F = 2·5 kg. For this inflation $m = 0·3$ kg. A payload of 16 kg., together with 10 balloons and the hydrogen, gives a total load of 33 kg. carried by 3 kg. of hydrogen. When a balloon bursts we assume that half the rubber (= 0·7 kg.) is blown off. The total decrease of W is thus 1 kg. The bursting level is assumed to be at 23 mb. With these data we construct Table II.

TABLE II

Number of Balloons ..	10	9	8	7	6
Total load : W ..	33	32	31	30	29
Mass of Hydrogen : m ..	3·0	2·7	2·4	2·1	1·8
Load/ kg. of Hydrogen : L_0 ..	11·0	11·8	12·9	14·3	16·1
Equilibrium pressure in millibars ..	..	..	25·0	38·0	Ground

The system has therefore two floating levels, and if the bursting level were higher there might be 3 or 4. In practice balloons vary in weight, some are weaker than others, and it is not possible to fill them all precisely to the same lift. The amount of rubber lost on bursting is also very variable, and there are cases where balloons develop pinholes and shrink slowly, so that no rubber is lost at all. For these reasons floating levels cannot be predicted accurately in advance, but the present results show that the flights behave substantially in the manner to be expected from this theory.

The rise in p_1 for high inflations does not occur with neoprene balloons when blown up to bursting point at the ground though the rubber balloons show it clearly. The difference is almost certainly a temperature effect. The manufacturers, in a private communication, have stated that neoprene 'freezes' or becomes less estensible at stratosphere temperatures. This would correspond to a large value of k in the above theory.

6. DETERMINATION OF PRIMARY FLUX

The experiments provided 4 sets of plates for analysis, obtained in flights 3, 4, 7 and 12. The plates of the brass stack in flight 12 showed stripping of the emulsion on development, and have not yielded satisfactory

measurements. The mean altitude in flight 3 was rather low, and though the plates are good, the primary tracks are too few to give a reliable determination. The results reported are therefore based on flight 4, and flight 7. Flight 4 was analysed at Bombay and flight 7 at Rochester.

Of the 80 plates from flight 4, the two end plates and two from the middle were scanned systematically for heavy tracks. When found, these were followed from plate to plate through the stack to distinguish primaries from slow secondaries. Primaries have an energy above the cut-off, which is approximately 6·5 Bev/nucleon at the geomagnetic equator, and at these energies the primaries pass completely through the stack unless they suffer nuclear collisions. The mean free path in the material of the stack is known to be 34·5 g./cm.^{2} for incident particles with $6 \leqslant Z \leqslant 10$, and 25·5 g./cm.^{2} for $Z > 10$. A break-up occasionally occurs in the emulsion, and the break-up products can often be recognised as alpha particles (4 times minimum ionisation) and singly charged particles (minimum ionisation). In such cases, a lower limit to the charge of the primary may be assigned from the break-up products.

δ-Ray measurements were made on all tracks for which Z could be assigned in this way with some assurance, and also on alpha particle tracks. The number of δ-rays in a standard length of track (100 μ) is given by the formula (Bradt and Peters, 1950 *c*).

$$N_\delta = AZ^2 + B.$$

From the results obtained from the known tracks, the constants A and B were evaluated, and the relation was then used to determine the charge on all the primary tracks found. As all the primaries have relativistic speeds the δ-ray count over a reasonable length of track, usually 1,000 μ or more, gives the value of Z. The uncertainty is of the order of one unit in Z. For analysis the tracks are divided into two groups (1) those for which $6 \leqslant Z \leqslant 10$ (generally called the C-N-O group), (2) those for which $Z > 10$. For each track the orientation and dip (with due correction for emulsion shrinkage) were recorded, these angles being then converted to true zenith angle and azimuth. The direction of travel is determined from the fact that a primary particle must be moving downwards.

Let z be the vertical axis normal to the plate. The zenith angle of the track is θ, and its azimuth, measured from the x, z plane, is ϕ. The dip β is the complement of the angle between the track direction and x. These angles are related by the equation

$$\sin \beta = \sin \theta \cos \phi.$$

Owing to difficulties of recognition, only tracks of a certain minimum projected length are included in the analysis. This is equivalent to the condition $\beta < \beta_0$. This implies that $\phi > \phi_0$,

where

$$\cos \phi_0 = \sin \beta_0 / \sin \theta.$$

When θ is less than β_0, all values of ϕ between 0 and $\pi/2$ are included, but when θ exceeds β_0 the permissible azimuth ϕ has the lower limit ϕ_0.

Consider an isotropic incident flux of N_0 particles per sq. cm. per sec. per sterad. The plate presents a projected area (A sin β), where A is the area of the plate, and the element of solid angle is $\sin \theta \, d\theta \, d\phi$. The rate of incidence on the plate at the angles θ, ϕ is therefore

$$n(\theta, \phi) = N_0 A \sin^2 \theta \cos \phi \, d\theta \, d\phi$$

Integrating over ϕ with the given limits, the rate of incidence for a given zenith angle becomes

$$n(\theta) = 2 N_0 A f(\theta) \, d\theta,$$

where

$$f(\theta) = \sin^2 \theta \text{ for } \theta \leqslant \beta_0$$

$$f(\theta) = \sin^2 \theta \left(1 - \sqrt{1 - \frac{\sin^2 \beta_0}{\sin^2 \theta}}\right) \text{ for } \theta > \beta_0.$$

To allow for the absorption in the atmosphere, $n(\theta)$ must be multiplied by a factor $e^{-h/\lambda \cos \theta}$, where λ is the mean free path in air, and h the vertical height of the atmosphere above the point of observation. h is known as a function of the time from the altitude curve, and the total number of tracks recorded at the zenith angle θ is thus given by

$$N_\theta = 2 N_0 A f(\theta) \, d\theta \int_0^T e^{-h/\lambda \cos \theta} \, dt.$$

Denoting the integral by $\phi(\theta)$, the total number of tracks recorded between any given limits of zenith angle is

$$N(\theta_1, \theta_2) = 2 N_0 A \int_{\theta_1}^{\theta_2} f(\theta) \phi(\theta) \, d\theta.$$

Some of the observed tracks represent particles which have had an appreciable path in the stack before reaching the selected plate. If the path in the stack is L, and the mean free path λ', each track must be assigned a statistical weight $e^{L/\lambda'}$. The appropriate value of $N(\theta_1, \theta_2)$ to employ is the sum of the statistical weights of all the observed tracks.

The analysis has been made for several plates of the stack, and for different values of β_0. High values of β_0 give smaller flux values, showing

that tracks (especially of the C-N-O group) are liable to be missed or excluded by the observer if the minimum projected length is too small. The value of β_0 finally adopted is 34°, corresponding to a minimum projected length of 300 μ in a 200 μ emulsion. With this criterion a single end plate has yielded 24 tracks, with a total statistical weight of 33.

Taking the mean free path in air of the C-N-O group as 27 g./cm.^{2} (Bradt and Peters, 1950 *c*), $\phi(\theta)$ is determined by treating the altitude curve as a series of sections of constant height. The product $f(\theta)\phi(\theta)$ is then tabulated at 10° intervals, and the integral is evaluated by quadrature. The procedure for the group $Z > 10$ is similar, except that the value 21 g./cm.^{2} is used for the mean free path in air, and the value 25·5 g./cm.^{2} for the mean free path in the material of the stack.

The tracks recorded in flight 4 show an apparent excess of particles coming from the south. This is almost certainly due to an unforseen tilt of the stack, which would cause an excess of particles to be recorded on the face tilted upwards. A tilt of some 10° would account for the observed asymmetry. Calculation shows that the total number of particles recorded in the tilted plate will not differ, within the limits of accuracy of this experiment, from the number recorded in a vertical plate.

The final values adopted, after considering these results and comparable results of flight 7, are as follows:

For $6 \leqslant Z \leqslant 10$, $N_0 = 1{\cdot}45 \pm 0{\cdot}30$ particles/m.^{2} sec. sterad

For $Z > 10$, $N_0 = 0{\cdot}33 \pm 0{\cdot}08$ particles/m.^{2} sec. sterad.

7. Charge and Angular Distribution

The charge specturm of the primaries has been determined by others at higher latitudes (Bradt and Peters, 1950 *a*; 1950 *c*). The present results agree with this in general, but some uncertainty in the δ-ray calibration and the relatively small number of particles observed make the specturm uncertain in detail. The relative intensity of the two groups of particles agrees well with previous observations.

For a major part of the duration of the flight, the plates remained under about 55 g./cm.^{2} of matter. The primaries have large collision cross-sections, and hence those at large zenith angles were completely cut off. This resulted in a relatively small observable E.W. asymmetry of the incoming heavy primary radiation. Thus, this asymmetry, in the present experiment, is within the statistical uncertainty of the results.

8. SUMMARY

The paper describes high-altitude balloon experiments with nuclear plates, made near the geomagnetic equator. A magnetic orientating unit was used. The behaviour of balloons is discussed, and it is shown that systems of balloons may have a series of stable floating levels at determinate altitudes. Analysis of the tracks observed in the plates has given the following values for the primary cosmic ray flux at the geomagnetic equator:

For $6 \leqslant Z \leqslant 10$, $N_0 = 1 \cdot 45 \pm 0 \cdot 30$ particles/m.^{2} sec. sterad.

For $Z > 10$, $N_0 = 0 \cdot 33 \pm 0 \cdot 08$ particles/m.^{2} sec. sterad.

Any observable E.W. asymmetry at the heights reached by the plates is within the statistical uncertainty of the results. The charge spectrum is in general similar to what has been previously observed.

9. ACKNOWLEDGEMENTS

These experiments were initiated and directed by Dr. B. Peters. Others who took part in the experiments were Messrs. R. R. Daniel, D. Lal, R. C. Murthy, G. S. Shrikantia, G. V. Vasudevachar, D. Venkat Rao, K. G. Vohra, and Yash Pal. We are grateful to Dr. M. F. Kaplon who provided us with results of the analysis of plates from flight 7. We are indebted to The Madras Christian College, The Vellore Medical College and The Central College, Bangalore, for facilities generously given, and to the Meteorological Department, All India Radio, and the Defence Department, Government of India, for their valuable help. The experiments were financed partly by the University of Rochester and partly by the Indian Atomic Energy Commission.

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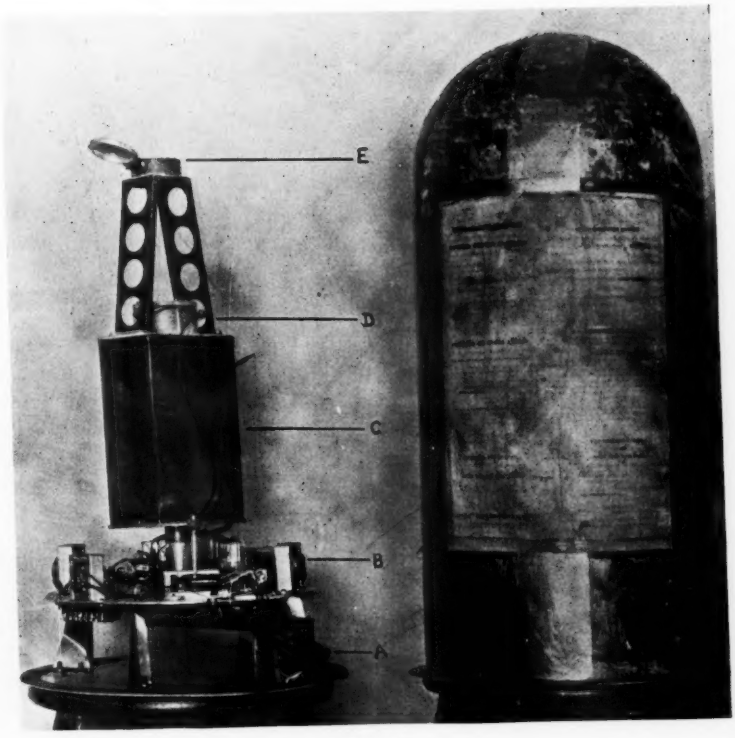

FIG. 1

THE INFRA-RED ABSORPTION SPECTRUM OF POTASSIUM CHLORATE CRYSTALS—Part II

By A. K. Ramdas

(*From the Raman Research Institute, Bangalore*)

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1. Introduction

In Part I, the author published the results of a study on the infra-red absorption by a single crystal of potassium chlorate in the range 1 μ to 15 μ, by means of a Beckmann infra-red spectrophotometer (model I R2). In the present investigation the work has been extended upto 22 μ using thinner crystals than formerly. The instrument itself had meanwhile been overhauled and its sensitiveness improved. The results now reported are therefore superior to those presented in Part I.

The crystals were studied, as before, with the flat face (001) perpendicular to the infra-red radiation, percentage transmission being read off directly with the instrument. Readings were taken at 0·1 μ intervals and at still closer intervals near absorption maxima. The percentage cut-off curves of two of them which show the absorption maxima most clearly have been reproduced in Fig. 1. Curve III represents the % cut-off of the specimen of thickness 0·15 mm. and Curve I of specimen of thickness 0·06 mm.

The following features are shown by the curves:

I. A sharply defined, strong absorption band with its maximum at 5·3 μ (1887 cm.$^{-1}$).

II. Two well-defined absorption maxima at 6·3 μ (1587 cm.$^{-1}$) and 6·9 μ (1449 cm.$^{-1}$) which are weak in comparison with the 5·3 μ band. In Part I of the paper, this doublet was not resolved and a rather broad band with its maximum at 6·7 μ was recorded. Coblentz (1906) to whom no reference was made in the previous paper through oversight had noticed these bands as also the one at 5·3 μ.

III. A very strong absorption band with a flat top, extending from 10 μ to 10·8 μ (1000 cm.$^{-1}$ to 926 cm.$^{-1}$).

IV. A medium strong absorption band at 13·5 μ (741 cm.$^{-1}$).

V. A strong and sharply defined absorption maximum at $16{\cdot}2\,\mu$ (617 cm.$^{-1}$).

VI. In the slope of the absorption maximum at $16{\cdot}2\,\mu$, we notice inflexions at $17{\cdot}25\,\mu$ (580 cm.$^{-1}$), $18\,\mu$ (556 cm.$^{-1}$), and $18{\cdot}75\,\mu$ (533 cm.$^{-1}$).

VII. A strong and sharply defined absorption maximum at $20{\cdot}3\,\mu$ (493 cm.$^{-1}$). This band shows indications of structure.

Schæfer and Schubert (1921) in their reststrahlen studies with pressed powder of $KClO_3$ found reflexion maxima at $10{\cdot}12\,\mu$ and $16{\cdot}12\,\mu$ which evidently are related to the absorptions referred to in III and V above.

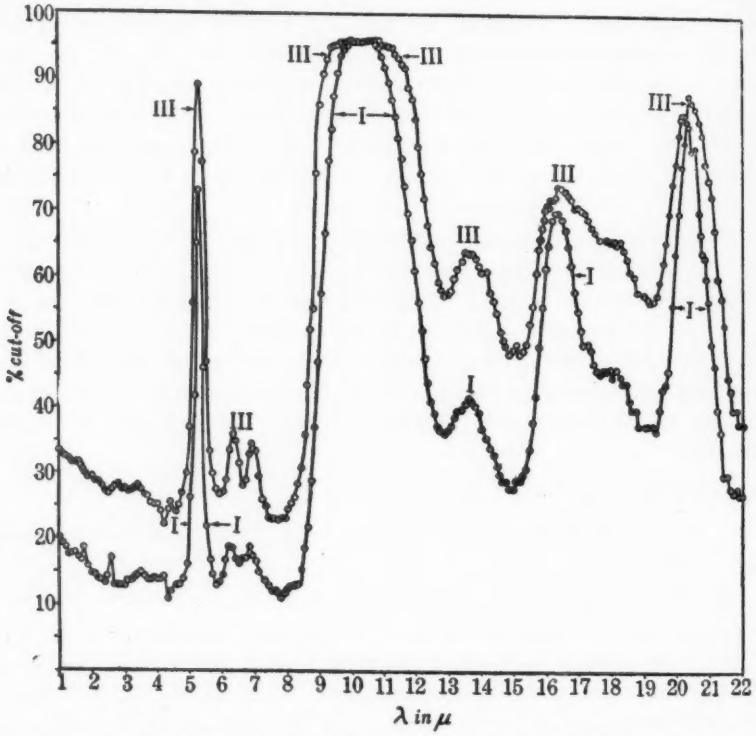

FIG. 1. Infra-red absorption spectra of single crystals of potassium chlorate.

2. INFRA-RED ACTIVE FUNDAMENTALS

In Part I, the absorption maxima in the infra-red were explained in a general way in terms of the characteristic frequencies of the chlorate ion the free state, *viz.*, ν_1 (930 cm.$^{-1}$) and ν_3 (620 cm.$^{-1}$) belonging to the totally

symmetric class A_1; ν_2 (975 cm.$^{-1}$) and ν_4 (486 cm.$^{-1}$) belonging to the doubly degenerate class E. But in the transformation from a free ion to a crystal, the number of internal vibrations increases because there are two molecules in each unit cell and the symmetry of the crystal structure (C_{2h}^2) removes the degeneracy of modes of the E class. The group analysis gives the number of internal vibrations and the selection rules as shown, in Table I.

TABLE I

Class	Number	Raman effect	Infra-red
A_1	4	Active	Inactive
A_2	2	Active	Inactive
B_1	2	Inactive	Active
B_2	4	Inactive	Active

i.e., there are six Raman active internal vibrations and six infra-red active, the two sets being mutually exclusive because of the presence of a centre of symmetry. We can picture the change in internal frequencies from a free ion to crystal as follows:

TABLE II

Free ion	Crystal	
Raman active and Infra-red active	Raman active	Infra-red active
ν_1 (A_1)	ν_1 (A_1)	ω_1 (B_2)
ν_3 (A_1)	ν_3 (A_1)	ω_3 (B_2)
ν_2 (E)	ν_2 (A_1), ν_2' (A_2)	ω_2 (B_2), ω_2' (B_1)
ν_4 (E)	ν_4 (A_1), ν_4' (A_2)	ω_4 (B_2), ω_4' (B_1)

Thus the infra-red and Raman frequencies would, strictly spreaking, be different.

The Raman effect in the powdered crystals has been studied by Krishnamurthi (1930) and Venkateswaran (1938), and by Shantakumari (1950) in a single crystal. Their results have been given in Table III.

TABLE III

Krishnamurthi (Powder)	Venkateswaran (Powder)	Shantakumari (Single crystal)	ClO_3^- ion
	915 (1)	920 (1)	
934·8	929 (10)	930 (10)	930
971*	977 (4)	975 (7)	975
..	615 (1)	620 (1)	615
482	478 (3)	486 (6)	480
	493 (0)		

* With two faint companions.

We notice that the Raman frequencies which have been reported fall into four main groups which approximate respectively to the four fundamental frequencies of the ClO_3^- ion. The results of the different authors are somewhat divergent, which may in part be ascribable to their having recorded the spectra in different circumstances. For our present purpose, we may ignore the splitting of the fundamental frequencies in the crystal shown in Table II and base our interpretation of the infra-red absorption data on four fundamental frequencies denoted as ω_1, ω_2, ω_3, ω_4 respectively, for which we assume the values 930, 975, 620 and 486 $cm.^{-1}$, these being the same as those observed in the Raman effect by Shantakumari.

3. INTERPRETATION OF RESULTS

On the assumptions made above, the following interpretations of the observed bands are put forward as the most probable (Table IV).

The bands IV and VI have been interpreted as combinations of the internal and lattice frequencies of the crystal. There are actually nine Raman active and six infra-red active lattice frequencies, the two sets being mutually exclusive. The selection rules permit combinations between infra-red active internal frequencies and Raman active lattice frequencies and *vice versa*. The infra-red active lattice oscillations are unknown. Shantakumari has recorded five lattice lines in Raman effect which we may denote

TABLE IV

Serial No.	Observed Absorption Maxima		Assignment	Calculated	
	$\lambda\mu$	cm.$^{-1}$		$\lambda\mu$	cm.$^{-1}$
I	5·3	1887	$\omega_1+\omega_2$	5·25	1905
II	6·3	1587	$\omega_2+\omega_3$	6·27	1595
	6·9	1449	$\omega_2+\omega_4$	6·84	1461
III	10–10·8	1000–926	ω_2	10·26	975
			ω_1	10·75	930
IV	13·5	741	ω_3+L_4	13·4	747
V	16·2	617	ω_3	16·13	620
VI	18·0	556	ω_3-L_1	17·7	566
	18·75	533	ω_4+L_1	18·5	540
VII	20·3	493	ω_4	20·58	486

as L_1 (54 cm.$^{-1}$), L_2 (82 cm.$^{-1}$), L_3 (98 cm.$^{-1}$), L_4 (127 cm.$^{-1}$) and L_5 (145 cm.$^{-1}$). Since the data regarding the lattice oscillations are incomplete, the assignments shown against IV and VI are necessarily somewhat conjectural.

Some interesting features are noticed as regards the relative intensities of the internal vibrations in Raman effect and infra-red. In Raman effect, all the workers have got 620 cm.$^{-1}$ line very weak. In fact, Krishnamurthi in his study of Raman effect in $KClO_3$ crystal powder and Venkateswaran in Raman effect in solution of $KClO_3$ failed to observe this line. On the other hand, corresponding to that line we notice a strong and sharp absorption in infra-red. The 486 cm.$^{-1}$ line which is strong in Raman effect is also strong in infra-red absorption. As regards 930 cm.$^{-1}$ and 975 cm.$^{-1}$, the indications are that the latter is more strongly active than the former in absorption, while in Raman effect, 930 cm.$^{-1}$ is stronger than 975 cm.$^{-1}$, though it has a comparable intensity.

I am very grateful to Prof. Sir C. V. Raman, F.R.S., N.L., for the encouragement and guidance he gave me during this investigation. My thanks are also due to the Investigator-in-charge C.S.I.R. Radiation Scheme, Poona, for his kind permission to use the infra-red spectrophotometer.

4. SUMMARY

Crystals of potassium chlorate exhibit strong absorption bands in the infra-red at $10\,\mu$–$10{\cdot}8\,\mu$, and at $16{\cdot}2\,\mu$ and $20{\cdot}3\,\mu$. These are identified with the active fundamentals at ω_1 (930 cm.$^{-1}$, $10{\cdot}75\,\mu$), ω_2 (975 cm.$^{-1}$, $10{\cdot}26\,\mu$), ω_3 (620 cm.$^{-1}$, $16{\cdot}13\,\mu$) and ω_4 (486 cm.$^{-1}$, $20{\cdot}58\,\mu$). It is noticed that ω_3 is quite strong, while the corresponding Raman frequency comes out very weakly. The vibration ω_1 is more strongly Raman-active than ω_2, while the reverse appears to be the case in the infra-red. Absorptions are also observed at $5{\cdot}3\,\mu$, $6{\cdot}3\,\mu$ and $6{\cdot}9\,\mu$ which are interpreted as first-order combinations among these four fundamental frequencies, while other bands at $13{\cdot}5\,\mu$, $18\,\mu$ and $18{\cdot}75\,\mu$ appear to be combinations of internal frequencies with low frequency lattice vibrations.

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PRELIMINARY OBSERVATIONS ON THE TEMPERATURE GRADIENTS AND LIGHT PENETRATION IN THE UPPER 200 FEET OF WATER OF THE BAY OF BENGAL*

By Raghu Prasad

(Central Marine Fisheries Research Station, Mandapam Camp)

Received December 13, 1951

(Communicated by Dr. N. K. Panikkar, F.A.Sc.)

Introduction

It is a common experience in the sea in low latitudes that insolation warms the upper layers, and that below a depth of about 100 meters there is usually a rapid fall in temperature. This lower layer of water with rapidly increasing density is known as the *thermocline* or *discontinuity layer*. The presence or otherwise of a thermocline has far reaching effects on the organic production and the distribution of planktonic organisms.

The earliest account of the temperatures at different levels of the Indian Ocean was given by Carpenter (1887) in which he gives the results of his observations in the Bay of Bengal. Schott (1902), Krümmel (1911), Matthews (1926) and Sewell (1932) have added to our understanding of the temperature gradients in the waters surrounding India. Still our present day knowledge on this subject is meagre.

Many devices have been invented for obtaining the temperature as a continuous function of depth but the bathythermograph designed by Spilhaus (1938) and later considerably modified by him, has overcome many of the difficulties that rendered previous designs ineffective. With the bathythermograph (Thermarine Recorder Model FA–190011) available at the Central Marine Fisheries Research Station it was decided to make observations on the temperature gradients whenever possible. Although the aim is to obtain a complete picture of the kaleidoscopic changes in the hydrological conditions throughout the year, owing to many difficulties it will only be possible at this stage to make intermittent observations and try to complete the picture in course of time.

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The following observations were made during a cruise from Trincomali to Madras, Calcutta, back to Madras and then to Mandapam. During the cruise observations on temperature gradients were made at 22 stations and water samples were collected at these stations as well as from another five stations (Fig. 1). The pH of these samples was determined on board the ship using Bromthymol blue as the indicator but the determination of salinity had to wait until the samples were brought back to the laboratory. The

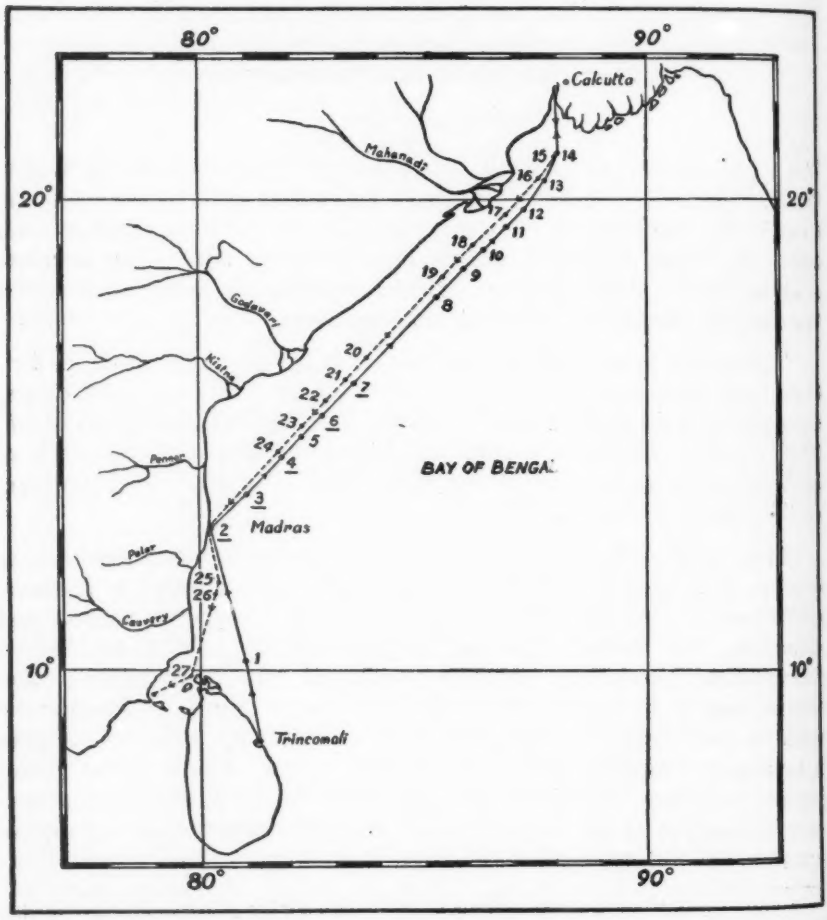

FIG. 1. Shows the stations at which observations were made. Numbers underlined indicate stations where bathythermograph readings were not taken.

salinity was estimated by the standard chlorinity titration method. Information such as the exact position, atmospheric temperature, barometric pressure, colour of water, nature of sea, depth and nature of bottom, direction and force of wind at the time of observation was also recorded in log sheets. At stations covered during day time, the penetration of sunlight was measured with the aid of a Secchi disc.

It may be mentioned here that the observations presented below are not to be regarded in any sense as a complete survey, but represent the first step in collecting adequate data for an understanding of the hydrological conditions of the water masses surrounding our peninsula.

In embarking on investigations of this kind it is necessary to call upon many persons for assistance and it gives me great pleasure to acknowledge the help received. This investigation, carried out on board I.N.S. *Delhi*, was made possible by the willing co-operation of the Navy and the Central Marine Fisheries Research Station. First and foremost amongst these, I wish to mention Rear-Admiral G. Barnard, Rear-Admiral Commanding the Indian Naval Squadron and Captain Chatterji to whom I tender my gratitude and appreciation. To the Naval Personnel who helped me in managing the bathythermograph and the Secchi disc I offer my sincere thanks.

Distribution of Temperature in the Upper 200 Feet of Water

Carpenter (1887) showed that from the surface to a depth of nearly 20 fathoms the temperature shows only little change but below this lies a zone extending downwards for more than the next hundred fathoms in which the temperature falls rapidly. Schott (1902) concluded from the data he had at his disposal that in the Indian Ocean the discontinuity layer lies at a depth below the surface which is intermediate between that found in the Atlantic and Pacific Oceans, *i.e.*, between 90 and 140 meters. He attributes the presence of this zone partly to the alternating effects of the seasons and partly also to the effect of lateral movements of the upper stratum which cause a thinning of the surface currents resulting in the deep lying colder and more saline water approaching the surface. Thus during hot weather the surface water becomes condensed and has a raised temperature but during the cold season this water cools and sinks down to a depth of 91 to 137 meters. Krümmel (1911), however, points out that true discontinuity layers in the other seas occur at a level that is only a few meters, 15 to 20 meters, below the surface which is caused by the heating up of the uppermost levels in summer and refuses to believe that this sudden change in temperature at depths as great as 100 meters can in any way be due to the heating up and evaporation of the surface water. He is of opinion that a sharply defined

thermocline is caused either due to the ascending movements of deep strata that carry cold water towards the upper levels, which have been warmed by the sun, or to horizontal movement of large masses of water due to the surface currents, the warm upper layer thus becoming sharply separated from the deeper colder water. Sewell (1932) suggests that in the Bay of Bengal the discontinuity layer may be produced in yet another manner, at least at certain seasons of the year, by the dilution of the surface water by rain or river water and thus by virtue of its reduced salinity and specific gravity it floats on the top of more saline water preventing usual convection currents setting up and restricting warming up by insolation to the upper stratum resulting in the formation of a discontinuity zone where two layers of unequal salinity meet. According to him the average temperature of the surface water, as calculated from all observations is 28·31° C. and, as a rule, there is only very little change in the upper 25 fathoms at which depth the average temperature is 26·75° C.

Sewell, *op. cit.*, has constructed a graph showing the upper and lower limits of the discontinuity zone throughout the year for the Bay of Bengal and the Andaman Sea. He also points out, however, that no data were available for the months of either August or September. The upper level, according to Sewell, for August is 40 to 50 fathoms and the lower limits for the same month being from 78 to 90 fathoms. But the observations recorded here for the month of August (August 9 to 29) show the existence of definite thermoclines at several places in the Bay of Bengal at comparatively low levels.

Schott (1902) has suggested that the thermocline should be defined as one in which the temperature changes by not less than 2° C. (3·6° F.) in 25 meters vertically. According to this defintion it will be noticed that there are well marked thermoclines developed within the upper 200 feet at several places during August (stations 8 to 11, 17 to 20, 25 and 26). The depths at which thermoclines develop vary from place to place and also from time to time. It is seen from Figs. 3 and 4 that at the stations 8 to 11 thermoclines developed approximately at 65, 65, 70 and 75 feet respectively, whereas at stations 17 to 20, 25 and 26 the thermocline was at 130, 90, 35, 60, 120 and 110 feet respectively (Figs. 8, 9, 11 and 12). It may be added here that at stations 12 to 16 (Fig. 1) one would not normally expect definite thermoclines in the upper 200 feet of water as there is likely to be considerable mixing up of water in the upper layers owing to the influx of large quantities of water brought down by the Ganges and Mahanadi (Figs. 5, 6, 7 and 8). In this connection it may be pointed out that the depths at which thermoclines developed at stations 8 to 11 gradually increase from 65 to 75 feet which may

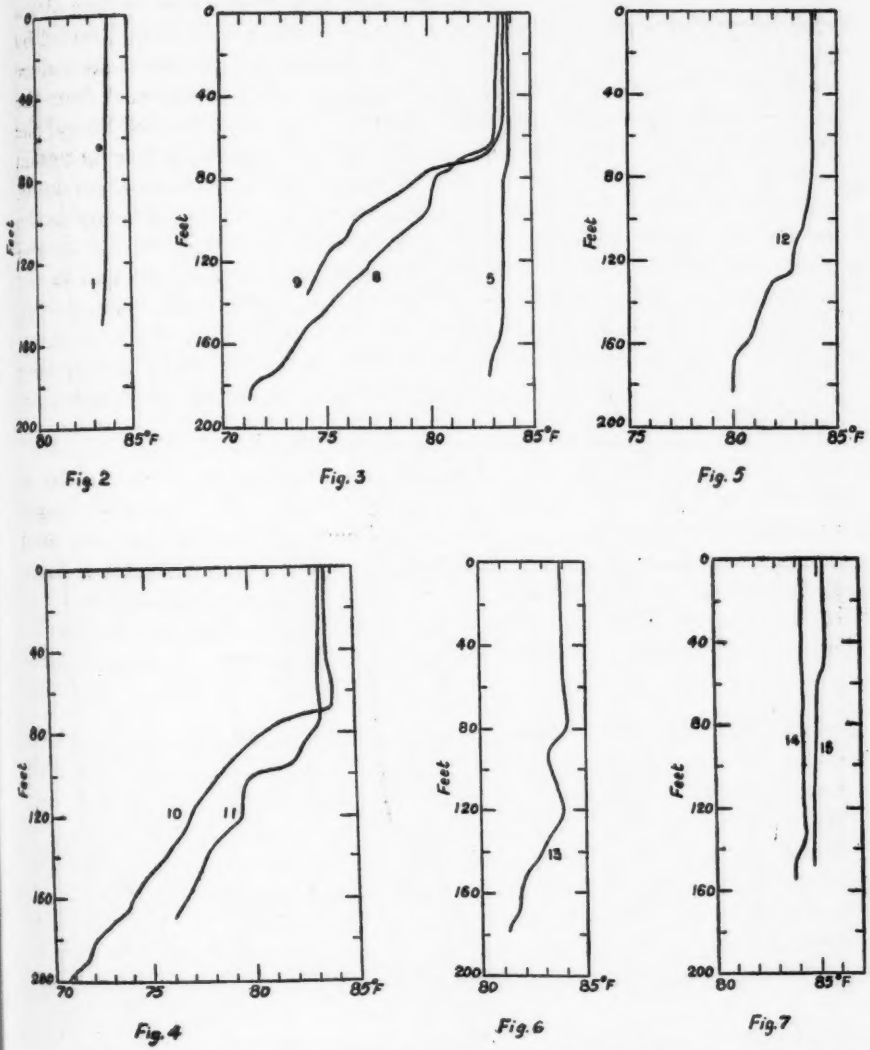

Fig. 2 Fig. 3 Fig. 5

Fig. 4 Fig. 6 Fig. 7

FIGS. 2–7. Show the distribution of temperature in different depths at ten stations. Number against each line represents station number.

indicate the spreading of a tongue of less saline and lighter water which, as is to be expected, thins out gradually. It is likely that thermoclines are developed at the stations mentioned above at the places where the two strata of

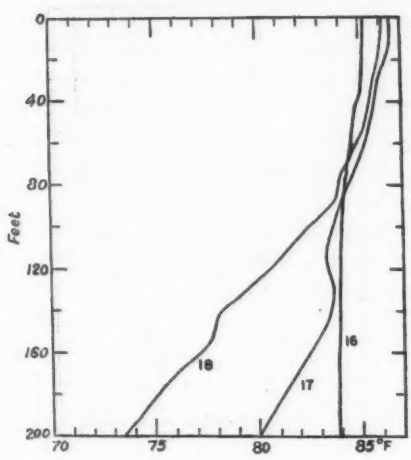

Fig. 8

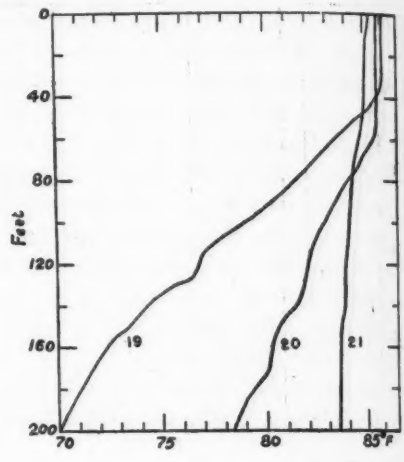

Fig. 9

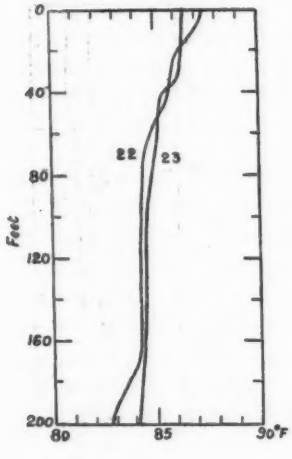

Fig. 10

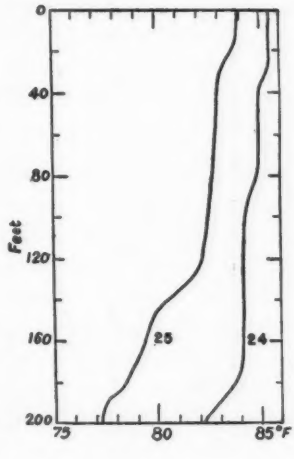

Fig. 11

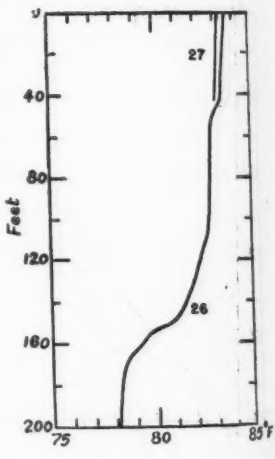

Fig. 12

FIGS. 8–12. Distribution of temperature at different depths at twelve stations in the Bay of Bengal. Number against each line denotes station number.

water of different salinity meet, as suggested by Sewell, and it is probable that thermoclines might have existed at deeper layers as we approach the mouths of the rivers. Again the thermocline at station 17 was at 130 feet,

the location of the station being near the mouth of Mahanadi, whereas as we move away from the river mouth it will be observed that the thermocline develops closer to the surface—90 and 35 feet at stations 18 and 19 respectively. Station 20 shows a thermocline at 60 feet while at the next four stations there are no thermoclines developed within the upper 200 feet (Figs. 9, 10 and 11). Thermoclines are developed at 120 and 110 feet at stations 25 and 26 respectively. The same explanation holds good for all these stations, *i.e.*, those located just opposite river mouths (21 to 24) do not show thermoclines within the 200 feet and at those places where the influence of river water is only slightly felt the thermoclines develop comparatively near the surface. It is of interest to note here that at stations 8, 10, 18 and 19 the difference in the temperatures between the surface and at 200 feet is about the same as the maximum difference observed in the fluctuation of the surface temperature in any month. According to Sewell (1929) the extreme range of surface temperature, *i.e.*, between the highest and the lowest recorded temperatures, in each month rises from 3·2° C. in April to 6·45° C. in December. The range in surface temperature recorded during this cruise is 4·02° C. (*ca.*, 7·23° F.). Stations 8 to 11 and 18 to 20 show this or greater difference in temperature between the surface and at 200 feet (Figs. 3, 4, 8 and 9). This may mean that the changes in the surface temperature may be brought about by the mere upwelling of the subsurface water but whether this phenomenon actually happens and also whether this is one of the contributing factors it is difficult to say at present.

Light Penetration

Another factor which is most important for organic production is radiation. It not only directly controls the phytoplankton production but is important indirectly through its effect on temperature. The light that is effective for phytoplankton growth depends, of course, on the transparency of the water. The light falling on the sea is continuously changing with time and thus the depth of photosynthetic zone varies throughout the day with the intensity of illumination. The transparency of the water plays a leading part in controlling the depth of the photosynthetic zone and similarly the relative position of the thermocline and the euphotic zone is also of considerable importance in organic production.

Factors such as the presence of debris and plant cells in large quantities increase the turbidity. In certain cases plant cells themselves may become abundant to cause a significant decrease in transparency. The extent to which plant cells may cut off light is shown by Clarke (1946) in which he has given the relation between the Secchi disc measurements and the abund-

TABLE I. *Oceanographic data collected during the cruise*

Date	Station number	Position		Time Hrs.	Surface temp. °C. 1/	Atmospheric temp. °C. 1/	pH 2/	Salinity ‰	σ_t	Depth (fm.)	Max. depth of visibility of Secchi disc. (ft.) 3/
		N. Latitude	E. Longitude								
9-8-1950	1	10°16′00″	81°02′00″	05 45	28·47	29·16	8·27	33·84	21·25	1210	48
10-8-1950	2*	13°08′00″	80°18′00″	06 00	26·67	25·56	8·07	34·76	22·66	..	..
do	3*	13°48′00″	81°01′00″	10 00	28·33	29·44	8·27	34·04	21·58	>1300	..
do	4*	14°37′00″	81°50′00″	14 00	28·33	29·72	8·27	34·01	21·56	>1300	..
do	5	15°06′00″	82°20′00″	16 30	28·75	30·00	8·37	33·73	21·21	>1300	62
do	6*	15°24′00″	82°37′00″	18 00	28·33	28·61	8·37	33·93	21·50	>1300	..
do	7*	16°11′00″	83°24,00″	22 00	28·05	28·89	8·17	33·94	21·60	>1300	..
11-8-1950	8	18°01′00″	83°16′30″	07 00	28·47	30·00	8·38	31·29	19·15	>1300	54
do	9	18°37′30″	85°56′00″	10 00	28·61	30·56	8·28	30·41	18·44	1233	48
do	10	18°57′00″	86°22′00″	13 00	28·61	29·72	8·28	29·85	18·03	1233	60
do	11	18°25′00″	86°46′00″	16 00	28·75	30·27	8·28	31·19	19·32	790	49
do	12	19°53′30″	87°12′30′	19 00	28·75	28·33	7·78	30·41	19·73	493	..
do	13	20°25′20″	87°38′30″	22 00	28·75	28·61	8·18	30·01	18·43	47	..
12-8-1950	14	20°55′00″	88°02′00″	01 35	29·02	28·33	8·38	31·29	19·30	30	..
22-8-1950	15	20°54′00″	88°00′01″	07 11	29·58	29·16	8·38	28·93	17·35	26	14
do	16	20°27′00″	87°33′00″	10 00	29·58	30·56	8·38	29·76	17·97	38	36
do	17	19°47′30″	86°52′00″	14 00	30·27	31·11	8·38	30·80	18·51	483	36
do	18	19°08′00″	86°03′30″	18 00	30·14	30·84	8·38	31·44	19·03	1182	..
do	19	18°27′30″	85°22′00″	22 00	30·14	28·89	8·18	31·39	19·00	1180	..
23-8-1950	20	16°44′00″	83°41′00″	07 00	29·86	28·33	8·37	33·27	20·49	>1300	33
do	21	16°15′00″	83°12′00″	10 30	29·58	29·16	8·37	33·61	20·85	>1300	78
do	22	15°45 00″	82°53′00″	14 00	30·69	30·00	8·37	33·64	20·49	1185	78
do	23	15°13′00″	82°19′00″	18 00	30·27	28·89	8·37	33·04	20·19	1182	..
do	24	14°39′00″	81°46′00″	22 00	29·72	29·05	8·37	33·15	20·46	>1300	..
28-8-1950	25	11°49′30″	80°27′00″	17 20	28·75	27·78	8·27	34·37	21·70	>1300	..
do	26	11°42′00″	80°22′00″	18 30	28·61	28·89	8·27	33·93	21·41	>1300	..
29-8-1950	27	09°52′00″	79°55′00″	06 30	28·47	26·67	8·37	35·10	22·41	7	..

* Stations marked with an asterisk indicate those at which water samples alone were collected.

1/ Readings were recorded in degrees Fahrenheit and have been converted to the Centigrade scale subsequently.

2/ Corrected for the salt error of the indicator.

3/ Average of depths at which the disc disappears and at which it appears.

ance of phytoplankton. In all cases in which plant pigments exceeded 40,000 Harvey units per m^3 the Secchi disc depth was found to be reduced to 8 meters or less.

In order to get an idea of the penetration of light in the Bay of Bengal limits of visibility tests were conducted with the aid of the Secchi disc. It will be noticed from Table I that the depth varies from 33 to 78 feet except at station 15. This station, as will be seen from Fig. 1 is located very close to the mouths of the Ganges and due to the influx of large quantities of mud-laiden water from the river, the transparency of water was reduced. Consequently the Secchi disc reading was only 14 feet. Owing to lack of facilities it was not possible to make plankton collections at any of these stations and hence the organic production in the euphotic zone could not be estimated.

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STUDIES ON TUBER HEMICELLULOSES

Part II. Hemicelluloses from the Tubers of *Asparagus racemosus* and Their Complete and Partial Hydrolysis

By P. S. Rao, F.A.Sc., and K. L. Gakhar
(*Forest Research Institute, Dehra Dun*)

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It has already been reported that the root powder (moisture content: 13·42 per cent.) of *Asparagus racemosus* Willd. contains 37·44 per cent. of free sugars and 2·10 per cent. of mucilages, while the total non-fibre carbohydrates amount to 52·89 per cent.[1] The other constituents of the non-fibre carbohydrates have now been examined and are found to be hemicelluloses (5·40 per cent.) and some insoluble polysaccharides (7·95 per cent.). The isolation and examination of the hemicelluloses are reported in this paper.

After the removal of saponins, free sugars, mucilages and pectins by successive treatments with ethyl acetate, 70 per cent. alcohol, hot water and ammonium oxalate solution, the root powder has been extracted for the isolation of the hemicelluloses with 4 per cent. sodium hydroxide according to the method of Norman.[2] On further fractionation as per the procedure of Norris and Preece,[3] the hemicelluloses have given rise to two fractions, namely, A_2 and B_2.

Both A_2 and B_2 are amorphous substances, which are almost white in colour with a greyish tinge. They are soluble in hot water, the solutions being slightly viscous but not mucilaginous. Further, they are readily hydrolysed by boiling dilute mineral acids, indicating their hemicellulosic nature.[4] They are composed of the same sugar and uronic acid, namely, glucose and galacturonic acid, but in different molecular proportions. In A_2 the molecular ratio of glucose to galacturonic acid is 10:1, while in B_2 it is 5:2.

The two hemicelluloses have been subjected to partial hydrolysis also. This degradation is best brought about by heating the material with 1·5 per cent. sulphuric acid for 3 hours on a boiling water-bath. It may be noted that direct boiling of the mixture under reflux even for a short time usually results in almost complete hydrolysis. Under the controlled conditions mentioned both A_2 and B_2 are hydrolysed to glucose and an aldobionic

acid. The latter has been isolated as its barium salt. On further hydrolysis it gives rise to *d*-glucose and *d*-galacturonic acid in equimolecular proportions.

It may be noted that the aldobionic acid present in the mucilage portion of these tubers is also a gluco-galacturonic acid.[5] It is interesting to note that in both the mucilage and the hemicellulose portions the aldobionic acids are composed of the same sugar and uronic acid; however, they differ in their resistance to hydrolysis by acids. The constitutional factors responsible for this difference are yet to be studied.

It is also interesting to note that amongst the three species of *Asparagus*, the tubers of which have been examined in some detail, *A. filicinus* does not seem to contain any hemicelluloses,[6] while the other two contain two fractions each.[7] Further, *A. adscendens* and *A. racemosus* differ as regards the nature of the sugars and also the uronic acids constituting the hemicelluloses. The hemicelluloses from *A. racemosus* are composed of glucose and galacturonic acid, while those of *A. adscendens* are constituted from xylose, glucose and glucuronic acid.

Experimental

Isolation and fractionation of the hemicelluloses.—The debarked root powder of *Asparagus racemosus* was extracted successively with ethyl acetate, 70 per cent. alcohol, warm water and 0·5 per cent. ammonium oxalate solution in order to remove saponins, free sugars, mucilages and pectins. The residual powder was worked up for the isolation of the hemicelluloses. It (100 g.) was heated with 4 per cent. sodium hydroxide (500 c.c.) at 45-50° C. for two hours with frequent shaking. The mixture was filtered through a fine muslin and the residue was twice again extracted with the alkali, taking the same volume each time. After clarification by repeated filtration through glass wool, the extract was treated with 10 g. of sodium hypochlorite and just acidified with hydrochloric acid. This treatment was to destroy the lignins, if present to any extent (method of Norman[2]). After 10 minutes when no more chlorine was evolved and when the hemicelluloses settled down, the supernatant liquid was decanted off and the rest centrifuged. The separated solid was washed first with small quantities of water, then with 60 per cent. alcohol and finally with hot absolute alcohol. It was then dried first in air and then in a desiccator. The yield was 5·40 per cent. on the weight of the debarked root powder taken.

The product was fractionated according to the method of Norris and Preece.[3] A 1 per cent. solution of the substance in 4 per cent. sodium

hydroxide (500 c.c. in volume) was treated with excess of glacial acetic acid and allowed to stand for 6 hours. The solid that settled down (Fraction A) was separated in a centrifuge, and washed successively with water and hot alcohol. Its yield on the basis of the root powder was 2·00 per cent. The mother-liquor (600 c.c.) was next treated with half its volume of ethyl alcohol, when Fraction B separated out as a greyish white substance. It was also isolated, washed and dried as Fraction A, and was obtained in 3·40 per cent. yield. On further treatment with excess of alcohol, the mother-liquor, left after the separation of B, did not give any more solid (Fraction C absent).

The above fractions were subjected to further fractionation. They were separately dissolved in hot 4 per cent. sodium hydroxide so as to form 1 per cent. solution and filtered through glass wool to remove the slight turbidity present. On treatment with Fehling's solution at the rate of 30 c.c. for every 100 c.c. of the alkaline solution, no precipitate separated out in either case, indicating the absence of Fractions A_1 and B_1. Hence the two hemicelluloses corresponded to Fractions A_2 and B_2 of Norris and Preece. On acidification, followed by the addition of excess of alcohol, the alkaline solutions precipitated the hemicellulose. Both A_2 and B_2 were purified by repeated dissolution in dilute alkali and reprecipitation by means of acid and alcohol. Three such treatments were required to get ashless products. The final yields of purified A_2 and B_2 were respectively 1·65 per cent. and 2·90 per cent. on the weight of the debarked root powder.

Hemicellulose A_2.—In the purified condition A_2 was greyish white in colour, and contained 9·26 per cent. of moisture. It was insoluble in alcohol acetone, ether, etc., but was soluble in hot water yielding viscous but non-mucilaginous solutions. In 0·5 per cent. aqueous solution its specific rotation at 18° C. was + 19·7°.

The hemicellulose contained uronic acid, as it responded to the naphthoresorcin test.[8] The uronic acid was quantitatively estimated according to the method of Dickson, Otterson and Link[9] and was found to be 8·8 per cent. on zero-moisture basis of the hemicellulose. It did not contain any methoxyl group or pentose.

The purified material (2 g.) was hydrolysed by boiling under reflux with 2 per cent. sulphuric acid (150 c.c.) for 2 hours. The hydrolysate was neutralized with barium carbonate, filtered and the filtrate examined for the sugars and the uronic acids adopting filter-paper chromatography (horizontal migration method of Rao and Beri.[10]) Only glucose and galacturonic acid could be detected. The identity of glucose was confirmed by the preparation of

its osazone with its characteristic crystal structure and melting point (204-206° C.). The identity of the uronic acid was also confirmed by the determination of the specific rotation of its barium salt $\{[\alpha]_D^{32.5°} = +24·8°\}$[11] and its oxidation with nitric acid of sp. gr. 1·15 to produce mucic acid.

Composition of Hemicellulose A_2.—Since the hemicellulose contained only glucose and galacturonic acid, and the latter was found to be 8·8 per cent., the composition of the hemicellulose might be taken to be glucose and galacturonic acid present in the molecular ratio of 10:1.

Hemicellulose B_2 and Its Composition.—This fraction too was similar to Fraction A_2 in its colour, amorphous structure and solubility. It contained 8·2 per cent. of moisture. Its specific rotation in 0·3 per cent aqueous solution was + 27·1° at 18° C. It also underwent easy hydrolysis with dilute boiling sulphuric acid. The hydrolysate was examined as in the case of hemicellulose A_2, and was found to contain the same sugar and uronic acid, namely, glucose and galacturonic acid. In this case, the sugar and the uronic acid were present in the ratio of 5:2.

Partial Hydrolysis of A_2 and B_2.—The purified hemicellulose A_2 (5 g.) was heated in a round-bottom flask with 1·5 per cent. sulphuric acid (150 c.c.) on a boiling water-bath (98° C. at Dehra Dun altitude), when it rapidly went into solution. The course of the hydrolysis was followed by noting the optical rotation at frequent intervals. After 3 hours, when there was no more change in the rotation, the solution was neutralised with barium carbonate in the hot, concentrated to a small volume (40 c.c.), filtered and then treated with 95 per cent. alcohol (100 c.c.). The precipitated solid and the filtrate were examined separately.

From the filtrate alcohol was distilled off under reduced pressure. The resulting aqueous solution did not show the presence of any oilgosaccharides, since on further hydrolysis it did not undergo any change in reducing power or rotation. It contained only glucose.

The precipitate (barium salt) was purified by repeated dissolution in water and precipitation by means of alcohol. After the third precipitation it was filtered, dehydrated using hot absolute alcohol and dried in a vacuum desiccator. It contained 16·40 per cent. of barium (estimated as barium sulphate) and liberated 9·89 per cent. of carbon dioxide on heating with 12 per cent. hydrochloric acid.[9] These data indicated that the substance was the barium salt of an aldobionic acid. [Barium aldobionate, $(C_{11}H_{19}O_{10}COO)_2Ba$, contains 16·21 per cent. of barium and liberates 10·38 per cent. of carbon dioxide]. The salt (2 g.) was further hydrolysed by

boiling with 3 per cent. sulphuric acid (200 c.c.) under reflux for 2 hours. As the separated barium sulphate did not interfere with the course of boiling, no attempt was made to remove it. On analysis the hydrolysate was found to contain only glucose and galacturonic acid in equimolecular proportion.

B_2 was also hydrolysed in the same way, and the same products were obtained.

SUMMARY

The hemicelluloses of the tubers of *Asparagus racemosus* Willd. have been isolated and chemically examined. Two fractions, *viz.*, A_2 and B_2 of Norris and Preece designation, have been obtained.

Both the fractions are constituted from the same sugar and uronic acid, namely, glucose and galacturonic acid but in different proportions. In hemicellulose A_2 the molecular ratio of these compounds is 10:1, while in B_2 it is 5:2. Under conditions of partial hydrolysis, both the fractions give rise to glucose and a gluco-galacturonic acid.

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